

TRANSPORT ROUTES OF POLYCHLORINATED  
BIPHENYLS (PCBs) IN AQUATIC ECOSYSTEMS

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"Jag har inte det blekaste minne av den dag då jag inhämtade den för mitt blivande levnadskall så nödvändiga skrivkonsten. Jag minns inte alls när jag lärde mig rita mitt första A, inte heller när jag lärde mig Fader Vår. Över huvud har jag inga klarare minnen av mina första litterära strävanden och prestationer. Men däremot står den dag då jag fick mitt första metspö och min första fisk, med all dess spänning och sinnesrörelse så klar för mig som hade det varit igår"

*Juhani Aho, Fiskelycka*





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#### ABSTRACT

The transport of PCBs in aquatic ecosystems was studied in laboratory model systems and in the field. The attention was especially focused on aquatic interfaces, e.g. the sediment/water boundary and the surface microlayer.

PCBs were transported from sediment to water by three processes: 1. bioturbation 2. gasconvection from anaerobic sediments 3. desorption. Less chlorinated biphenyls, i.e. tetrachlorobiphenyls, were more easily desorbed from sediment to water than higher chlorinated ones. Hexa- and octachlorobiphenyls were transported to water mainly by bioturbation.

PCBs released from sediment to water were taken up by fish, presumably as a result of water/fat partitioning. The partitioning process was also indicated by the direct linear uptake of PCBs in chironomids.

The sedimentation of PCBs was measured in two southern Swedish lakes and in a bay in the southern Baltic. The  $\text{m}^{-2}\cdot\text{month}^{-1}$  rates were similar at the three locations and ranged from 1.2 to 10.9  $\mu\text{g PCBs}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ . The source for PCBs in sedimenting material was probably the atmosphere.

The transport of PCBs from water to air includes volatilization and jet drop transport. Less chlorinated biphenyls were volatilized to a higher extent than more chlorine-substituted ones.

In addition to the abiotic transport from water to air there exist biological processes that may transfer PCBs from sediment to water and to air. By aquatic insects whose larval stage live in contaminated sediment, PCBs and other chlorinated hydrocarbons are transported to air when the insects emerge.

The results of the study suggest that contaminated sediment of lakes and oceans act as a source for PCBs to water, biota and air.

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The thesis is based on the following papers:

- I. Transport of PCBs in aquatic laboratory model ecosystems from sediment to the atmosphere via the surface microlayer. Ambio, 11, 41-45, 1982 (co-author A. Södergren).
- II. Transport of  $^{14}\text{C}$ -labelled PCB compounds from sediment to water and from water to air in laboratory model systems. Water Research, in press.
- III. Uptake of sediment released PCBs by the eel (*Anguilla anguilla*) in static model systems. Presented at Oikos III conference on ecotoxicology in Copenhagen, 1982. Submitted to Ecological Bullentin.
- IV. PCBs (Clophen A 50) change composition when transported from sediment to air in aquatic model systems. Submitted to Environmental Science and Technology.
- V. Transport of PCBs from aquatic to terrestrial environments by emerging chironomids. Environmental Pollution, in press.
- VI. Sedimentation of polychlorinated biphenyls (PCBs) in limnic and marine environments. Submitted to Water Research.

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## 1. Background

When I began as a doctoral candidate in 1978 the following objectives were laid down to guide my thesis work: 'To clarify the mechanisms and the extent to which organic compounds toxic to the environment, especially PCBs, are adsorbed/desorbed to respectively from the sediment in aquatic environments. The transport of PCBs from sediment to water and air shall be examined, especially the PCB transport via the surface microlayer to the atmosphere'. The following hypothesis were put forward:

1. Contaminated sediments act as a source of PCBs to water and biota.
  2. The rate of release from sediment to water is dependent on the sediment properties and activity of benthic organisms.
  3. PCBs are transferred from water to air.
  4. The properties of the surface microlayer is decisive for the transport rate of PCBs from the water column to the air.
- The objectives established in this research plan have been valid during the whole study period.

## 2. Introduction

Why focus interest on a chemical group like polychlorinated biphenyls, that have been so extensively studied during the past 15 years (e.g. Hutzinger et al. 1974, Beeton et al. 1979)? The answer to the question is to be found within the question itself. The well documented, unique chemical/physical properties of PCBs make the compounds suitable for transport studies in model systems in the laboratory as well as in the field. The properties of PCBs, of which the most important are persistence and lipophilicity, make the chlorobiphenyls 'classical' pollutants in the environment (Jensen 1974). Since the compounds are very stable, resistant to both strong acids and bases, the matrix surrounding PCBs (like sediment or tissue) are easily 'burned' away. Neither are the PCB compounds metabolized or degraded to a higher extent. The analytical procedures are thus simplified and the efforts of the investigator can instead be spent on, for instance, ecological/ecotoxicological problems.

Sediments of lakes are mirrors of lake development as well as of recent human contamination (Digerfeldt 1972). The use of persistent, organic compounds in industry and agriculture, the discharge of heavy metals or the acidification of the environment are reflected in the sinks of the ecosystem, the sediment of lakes and oceans (Soutar et al. 1977, Niemistö and Voipio 1981, Norton and Hess 1980, Renberg and Hellberg 1982). But is sedimented or dumped persistent chemicals really incorporated and trapped in the sediment forever, or is there a redistribution to the water making the compounds again available to the aquatic biota? Which routes of abiotic transport exist from sediment to water and from water to air? What are the rates of the transport?

### 3. Transport routes of PCBs

That persistent, organic compounds like PCBs are taken up by the aquatic biota is well known. Several effects of the uptake have been proved, such as reduced photosynthesis in phytoplankton (Mosser et al. 1972, Harding 1976, Biggs et al. 1978), reduced productivity of zooplankton (Wildish et al. 1970, Maki and Johnson 1975), disturbed metabolic functions in fish and reduced hatching of roe (Desiah 1971, Bengtsson 1980) and disturbed reproduction in birds of prey and aquatic mammals (Helle et al. 1976, Olsson 1982, Helander 1983). However, the mechanisms of the uptake are not established nor the transport between abiotic compartments of the aquatic ecosystem. This is especially true for transport of the compounds from water to air, the vertical transport in the water column, their sorption or incorporation to the sediment and further redistribution to the water. The direction of these flows and to what extent the compounds are transported is essential for the understanding of the total flow within the aquatic ecosystem.

#### 3.1 Redistribution of PCBs from contaminated sediments

The importance of sediment/water interactions on the water chemistry of lakes is well documented. Chemical and biological processes in the sediment may reactivate previously sedimented compounds and make a transport back to the water possible. The properties of the interface between sediment and water, the

surface sediment, is therefore of uttermost importance for the transport processes. Nutrients, especially phosphorus, enriched in the sediments during periods of sewage discharges are under certain conditions (reduced, anaerobic conditions) mobile and pollute the water phase long after the discharges have been terminated (load of internal phosphorus).

Once deposited in the sediment, PCBs and similar chlorinated hydrocarbons are assumed to be inactivated. This is due to their hydrophobic and non-ionic nature that predict strong binding to the sediment. However, several mechanisms exist that redistribute PCBs from the sediment to the water (I, II, III):

1. Desorption, i.e. the partitioning of PCBs between sediment and water. Less chlorinated biphenyls (i.e. tetrachlorobiphenyls) are more readily desorbed from sediment than higher chlorinated ones. In a 10-week experiment about 0.4 ug/l of tetrachlorobiphenyl was found in the water while for hexa- and octachlorobiphenyl the concentration was below 0.1 ug/l. The sediment concentrations of PCBs were approximately 4 ug/g (fresh weight, II). The process seems to be of minor importance (Fisher et al. 1983) but may contribute to the uptake of PCBs in aquatic biota. The continuous uptake of PCBs by phyto- and zooplankton (thus eliminating the compounds from the water) maintain a flow of the chlorobiphenyls from sediment to water and shifts the partitioning of PCBs towards the water. The quality of the sediment, like organic content, content of lipids and proteins, number of bacteria and degree of decomposition is of major importance in the transport (II).
2. Gas convection. Gas produced in the sediment under anaerobic conditions will release particles to which PCBs are adsorbed (I).
3. Bioturbation. The macroinvertebrate activity in the sediment will result in a transport of PCBs to the water (I, II, III). From a sediment containing about 1 ug PCBs/g (fresh weight),  $0.2\text{--}0.7 \text{ ug PCBs} \cdot \text{l}^{-1} \cdot \text{week}^{-1}$  were transported to the water (III). The transport is a result of: a. The 'cultivation' of the sediment by the invertebrates and the deposition of faeces on the sediment surface. b. The mineralization rate of the sediment is raised by the activity of the invertebrates. A minerogenic sediment has lower capacity to adsorb PCBs, than a more organogenic one. c. The contact area of the sediment

surface towards the water is enlarged by the burrowing of for instance chironomids and tubificids. Interstitial water and particles containing PCBs are mixed with the overlying water.

### 3.2 Sedimentation of PCBs

Sedimentation of suspended particles in the water column of lakes and oceans may be estimated by the use of sediment traps. From these measurements, the flux of chlorinated hydrocarbons to the sediment is approximated (VI). The information obtained may reflect the contamination situation in the overlying water in a more representative way and on a longer time scale than would discrete sampling over short time intervals (Soutar et al. 1977).

The sedimentation rates of PCBs in two southern Swedish lakes (Lake Ivösjön and Lake Vombsjön) and a coastal bay in the southern Baltic (Hanö Bight) were determined in 1980-82 (VI). The rates were similar at the three locations and ranged from 1.2 to 10.9  $\mu\text{g PCB} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$  during summer. The source for PCBs in sedimenting material was probably the atmosphere. PCB concentrations in sedimenting material were higher than those in surface sediment. This may have been caused by a higher overall input of PCBs during recent years, but restrictions on PCB use make this rather improbable. A more likely explanation is that PCBs deposited in the sediment are mobile and may be recycled to the water (and thus lowering the PCB concentrations in the sediment).

### 3.3 The relevance of interfaces

An interface is defined as a boundary surface that separates two homogenous, physical/chemical distinctive parts of a heterogenous system. The important interfaces in aquatic environments are sediment/water and water/air. Also the boundary particle/water and water/organism (cell membrane, gill membrane) may be seen as interfaces. Processes at interfaces, that either delay or enhance the flow of PCBs are of importance for the



total flows between different compartments of the aquatic ecosystem. Since the aquatic interfaces have different properties (a lipophil, adsorptive character) compared to the media (water, air), lipophilic compounds like PCBs tend to accumulate (I, II, III, IV). Processes that enhance transport of PCBs across interfaces are bioturbation in the boundary sediment/water and jet drops in the surface microlayer.

The interfaces surrounding organisms are of special importance in ecotoxicology. It has been questioned whether the uptake of organochlorine residues in aquatic animals is governed by accumulation via the food chain (biomagnification, Risebrough and deLappe 1972), or as a partitioning process between water and the fat of the animals (III, Hamelink et al. 1971, Clayton et al. 1977). The different theories are substantiated with strong arguments. It may be speculated if this question of uptake simply is a question of exposure. In natural ecosystems, waters have a concentration of PCBs in the range of  $\mu\text{g}/\text{m}^3$  while the concentration in air only is  $\text{pg}/\text{m}^3$ . Thus a difference in concentration of  $10^6$  is present between water and air. Supposing, for simplicity, that the breathing rate of aquatic and terrestrial animals are in the same order of magnitude (or at least that the difference in breathing rate are considerably lower than  $10^6$ ) and that all PCBs exposed to the animals via the water and air breathed are taken up. Then, consequently, aquatic animals are exposed to a higher concentration of PCBs than terrestrial. Thus, higher levels of PCBs are obtained in aquatic animals as a result of partitioning between the medium and the fat pool compared to terrestrial organisms. If terrestrial animals have similar PCB levels as aquatic, another way of input of PCBs must dominate, namely input from food. In aquatic organisms the food-chain transport of PCBs and its results will be shielded by a high partitioning and perhaps only seen in animals of high age (exposed for the food-chain transport over a long time).

Animals, like seals and white-tailed eagles, living and feeding at interfaces between water and air will thus get the partitioning effect indirectly in the form of food (fish that has established an aquatic partitioning of PCBs, higher than

terrestrial organisms of similar trophic level). Elimination, however, will not be governed by aquatic partitioning and the compounds are kept in the body-fat of these predators. Accordingly, higher concentrations of PCBs are to be expected in these 'interface' predators compared to predators solely of aquatic or terrestrial ecosystems.

PCBs released from the sediment to the water were taken up by fish presumably as a result of water/fat partitioning (III). The process was also indicated by the direct linear uptake of PCBs from sediment of different PCB concentrations in chironomid larvae (V).

### 3.4 Transport of PCBs to air

Atmospheric transport of PCBs seems to be of great importance in contamination of the global ecosystem (Beeton et al. 1979, Giam et al. 1980 ). The most evident sources of atmospheric PCBs is the combustion of PCB-containing materials and the release of PCBs from industries. However, the question has recently been raised whether large contaminated water bodies, like Lake Michigan, can act as a source rather than as a sink (Doskey and Andrén 1981).

The transport of PCBs from water to air includes volatilization (IV) and jet drop transport (I, II, IV). When Clophen A 50 (a mixture containing about 50 PCB compounds) is transported from sediment to water and volatilized to air the composition of the PCB mixture is changed (IV). Less chlorinated PCBs are volatilized to a higher extent than more chlorine-substituted biphenyls. This may lead to a decreased exposure to aquatic organisms of less chlorinated PCBs, and consequently a higher uptake/partitioning of more chlorine-substituted biphenyls in the animals. Accordingly, it would give an alternative or additive explanation for the presence of more chlorinated biphenyls in aquatic organisms, that has hitherto been explained by metabolism of less chlorinated PCBs (IV).

Jet drop transport could include at least two processes whereby

lipophilic compounds are removed from the water to air:

1. Solved or emulsified compounds adsorb to rising microbubbles in the water. 2. Particles, to which the compounds are associated, adsorb to rising microbubbles. The bubbles collapse in the water/air interface and eject jet drops containing the solved compounds or particles. Jet drops may also eject compounds enriched in the surface microlayer (IV).

In lakes and oceans, microbubbles are generated from the sediment, from biota or through the action of waves (Garret 1970). In coastal areas of the ocean the amount of microbubbles in the range of 17-60  $\mu\text{m}$  was  $2.7 \cdot 10^4/\text{m}^3$  (Johnson and Cooke 1979).

No such information is available for lakes. Bubble formation and the rising of bubbles to the surface microlayer may also enhance volatilization of PCBs (IV).

In addition to the abiotic transport mechanisms, there exist biological processes that may transfer PCBs across the sediment/water and water/air interfaces. By aquatic insects (e.g. chironomids), whose larval stage live in contaminated sediments, PCBs and other chlorinated hydrocarbons are transported from the sediment to air (V). The compounds are taken up in the sediment by the larvae, transferred through the water column by the pupae and transported to the air and the terrestrial ecosystem by the emerging imagines. Particle feeding chironomids may dominate the limnic, profundal bottom-fauna (Jon  sson 1972). Consequently, chlorinated hydrocarbons present in adult chironomids may contribute in the diet of insectivorous birds, seasonally, when the birds are feeding primarily on these insects. Aquatic insects could thus act as a link between deposited persistent pollutants in the sediment of aquatic environments and terrestrial predators.

#### 4. Conclusions

Contaminated sediments act as a source for chlorinated hydrocarbons to the water. In the water the compounds are either taken up by the biota, transferred to the surface microlayer and air or will again sediment. Benthic macroinvertebrates will

take up pollutants from the sediment and may serve as food for benthic fishes, linking the organic, persistent compounds deposited in the sediment to the aquatic predators. Benthic insects transport the compounds from aquatic sediments to terrestrial environments when emerging.

Sedimented or dumped persistent pollutants will thus not be trapped in the depth of aquatic environments forever, but is recycled from the sediment and transferred to water and air. Though sediments are mirrors of human contamination, the mirrors not only reflect the contamination situation of the past, but turn into sources and influence on our present levels of contamination in the ecosystem.

## 5. Future research

Since most of my work has been performed in the laboratory (I-IV), the results of the experiment are to be confirmed in the field. Transport studies regarding persistent, organic compounds are almost impossible to carry out in lake ecosystems, because of difficulties in separating the PCB compounds desorbed/transported from the sediment to water from existing, circulating PCBs in the water column and food-web. Therefore, half-scale experiments in large out-door ponds (50 m<sup>3</sup>), similar in structure to the laboratory model systems, are chosen for verification. Preliminary results from these ponds confirm the principles and mechanisms of PCB transport acquired in the laboratory experiments.

## 6. Tack

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# Transport of PCBs in Aquatic Laboratory Model Ecosystems from Sediment to the Atmosphere via the Surface Microlayer

## Report

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PCBs that contaminate aquatic environments settle to the bottom through particle sedimentation and are eventually incorporated into the sediment. Owing to their chemical properties, it is not likely that they are again released to the water. To determine if bottom living organisms affect PCBs deposited in lake sediment, laboratory model systems comprised of *Chironomus* sp and/or *Tubifex* sp, water and sediment were incubated with PCB compounds. PCBs added to the sediment were taken up by the organisms but also redistributed within the sediment and released to the water and on to the surface microlayer. PCBs were transported from the water to the air via jet drops from bursting bubbles in the microlayer. A similar pattern of redistribution was caused by gas that developed in the sediment of anaerobic systems. Most of the PCBs that were relocated within the systems were apparently adsorbed to particles. If these results are applicable to conditions in the field, an additional pathway in recirculation of PCBs in the environment has to be considered, with the sediment acting as a source rather than a sink.

Polychlorinated biphenyls (PCBs) that contaminate aquatic environments originate from several sources, including precipitation, land runoff, industrial and municipal waste discharges and accidental spills. After introduction into aquatic ecosystems they are dissolved in the water, adsorbed on to various particles or accumulated in different trophic levels. Through particle sedimentation the compounds settle to the bottom (1) and are eventually incorporated into the sediment, from which they are assumed not to be released. If this is true, the sediment of lakes and oceans will act as the ultimate sink for these persistent substances.

Owing to their physical and chemical properties it is not likely that PCB compounds will be released to the water after incorporation into the sediment. However, a redistribution may occur. Important mechanisms that control the partitioning of PCBs between sediment and water are 1) erosion of the sediment 2) changes in physical parameters and chemical conditions in the water and/or the sediment 3) biotic transport induced by macroorganisms (chironomids, oligochaetes, molluscs, etc.).

Olsson (2) showed that erosion causes a redistribution of PCBs in river sediment. That salinity and temperature affect the

partitioning of PCBs between water and sediment was suggested by Pionke and Chesters (3) and Clayton (4). The role of bottom-living organisms, however, is not known. They may affect PCBs stored in the sediment either by burrowing or by consuming sediment particles. It is well known that the distribution of materials in sediment is influenced by macroorganisms and that substances are transported across the sediment/water interface (5, 6, 7, 8). Tubificids can transport sediment particles amounting to four to six times their own weight (9) in one day. Davis (10) showed that tubificids burrow to a sediment depth of at least 20 cm. Chironomids are usually found in the upper five cm (11, 12).

Courtney and Langstone (13) and Elder (14) showed that bottom-living organisms are able to remobilize and accumulate PCB compounds from contaminated sediment. Weiniger (15) concluded that a substantial portion (greater than 50 percent) of PCBs in pelagic carnivorous fishes in Lake Michigan is apparently recycled through bottom sediment at least once.

Under anaerobic conditions, PCBs may be released from sediment to water by gas convection induced by microorganisms. This could be of great importance for movement of materials across the sediment/water interface (5). These gas bub-

bles and bubbles produced in the water column burst at the water surface and inject into the atmosphere chemical substances, particles and bacteria (16, 17). It is known that PCBs occur in the microlayer of oceans and lakes (18, 19) but little information is available on how these compounds enter and leave the microlayer.

To study the effects of bottom-living organisms and anaerobic conditions on the distribution of persistent compounds in aquatic model ecosystems, PCBs were added to systems of different complexity, and transport to various compartments was followed. Jet drops from bubbles bursting at the water/air interface were collected to study their role as PCB carriers.

## MATERIALS AND METHODS

### Sampling

Sediment and water were taken from the eutrophic Lake Havgårdssjön, situated in the southern part of Sweden. Chironomids (*Chironomus plumosus* type) and tubificids (*Tubifex* sp) were collected in nearby Lake Vombsjön. The mean levels of PCBs were 35 ng/g in chironomids and 55 ng/g in tubificids, wet weight.

Havgårdssjön is located in an agricultural district; the watershed area is cultivated but the lake is not polluted by sewage effluents. The bottom consists of sand in the shallow parts and gyttja in the deeper areas. Sediment (mainly gyttja) was collected at a depth of about 3 m with an Ekman dredge. Sediment cores were taken with a Kajak-type corer (20) and were studied without being removed from the tube sampler (Figure 1). These sediment cores were regarded as undisturbed.

### Experimental set-up

The study was performed at 5°C and 18°C in the dark. Sediment collected with an Ekman dredge was sieved through a net (mesh size 3 × 3 mm) and aliquots (ca 600 ml) were poured into 2-liter glass beakers. The water content of the sediment was 71–84 percent, and loss of ignition was 16–

33 percent of the dry weight. 1400 ml of filtered lake water (Whatman GF/C) was carefully poured onto the sediment to a height of about 15 cm above the sediment surface. Undisturbed cores (450 ml sediment, 500 ml water) were left in the tubes in which they were taken. Organisms were added in numbers which simulated conditions in eutrophic lakes (Table 1).

The systems (except those kept anaerobic) were oxygenated with a stream of air (3-5 bubbles/second, about 1-3 mm in diameter) introduced 10 cm above the sediment surface. Transport of added compounds from the water to the air by jet drops was followed by collecting the drops on a teflon impactor (50.2 cm<sup>2</sup>) 7 cm above the surface of the water.

In systems incubated at 5°C the impactor tape was sampled weekly. The surface microlayer was also sampled weekly using a teflon plate (19). After six weeks the experiment was terminated and sediment, organisms and water were analyzed for added compounds.

In systems incubated at 18°C sampling of sediment, organisms, water, surface microlayer and jet drops was done after 8 weeks.

To study the partitioning of PCBs between water and sediment in a long-term

experiment, Clophen A 50 (a mixture of PCBs) was injected into sieved sediment in systems fixed with HgCl<sub>2</sub>. This water/sediment system was stored at 5°C for three years in the dark.

A summary of the experimental design is given in Table 2.

#### Substances studied

When the sediment to be incubated at 5°C had settled, 2, 3, 4, 4'-tetrachlorobiphenyl (120 µg), 2, 3', 4, 4', 5-pentachlorobiphenyl (120 µg) and Clophen A 50 (219 µg) were added. The substances were dissolved in 400 µl of ethanol and injected into the sediment via silicon septa in the walls of the beakers and tubes (Figure 1). The substances were injected into the sediment at four different places 5 mm below the sediment surface. The technique enabled an injection without disturbances of the sediment or contamination of the overlying water column.

Sediment for incubation at 18°C was treated as above. However, only Clophen A 50 was injected 20 mm below the sediment surface at six different places. 64 µg and 15 µg of Clophen A 50 were dissolved in 500 µl of ethanol and added to sieved and undisturbed sediments, respectively. Sieved systems received greater amounts

Figure 1. Experimental set-up to study movement of PCBs to the water and air from undisturbed sediment cores.

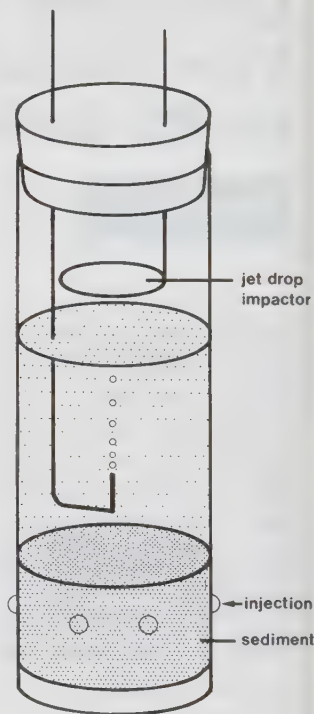


Table 1. Number of organisms added to the systems incubated at 18°C.

| Systems containing                                            | Number of organisms added |                            | Organisms/m <sup>2</sup> |                            |
|---------------------------------------------------------------|---------------------------|----------------------------|--------------------------|----------------------------|
|                                                               | Sieved sediment           | Undisturbed sediment cores | Sieved sediment          | Undisturbed sediment cores |
| <i>Chironomus</i> sp                                          | 35                        | 20                         | 3 800                    | 5 200                      |
| <i>Tubifex</i> sp                                             | 70                        | 40                         | 7 600                    | 10 400                     |
| <i>Chironomus</i> sp and <i>Tubifex</i> sp                    | 20 + 40                   | 15 + 30                    | 2 200 + 4 400            | 3 900 + 7 800              |
| <i>Chironomus</i> sp, <i>Tubifex</i> sp and <i>Valvata</i> sp | 20 + 40 + 15              | 15 + 30 + 15               | 2 200 + 4 400 + 1 600    | 3 900 + 7 800 + 3 900      |

Table 2. Substances and macroorganisms added and treatment of laboratory model ecosystems. Fixed systems were obtained by adding 5 ml 5% HgCl<sub>2</sub> to the water. Systems were made anaerobic by bubbling the water with N<sub>2</sub>. Number of replicate systems (if more than one) is given in parentheses.

| Treatment                                                                       | Sieved sediment incubated at 5°C |                       |                       |                    | Undisturbed sediment cores incubated at 5°C |                       |                       |                    | Sieved sediment incubated at 18°C |                    | Undisturbed sediment cores incubated at 18°C |                    |
|---------------------------------------------------------------------------------|----------------------------------|-----------------------|-----------------------|--------------------|---------------------------------------------|-----------------------|-----------------------|--------------------|-----------------------------------|--------------------|----------------------------------------------|--------------------|
|                                                                                 | Clophen A 50                     | Tetra-chloro-biphenyl | Penta-chloro-biphenyl | No substance added | Clophen A 50                                | Tetra-chloro-biphenyl | Penta-chloro-biphenyl | No substance added | Clophen A 50                      | No substance added | Clophen A 50                                 | No substance added |
| System                                                                          |                                  |                       |                       |                    |                                             |                       |                       |                    |                                   |                    |                                              |                    |
| System containing <i>Chironomus</i> sp                                          | X(3)                             | X                     | X                     | X                  | X                                           | X                     | X                     | X                  | X(2)                              |                    | X(2)                                         |                    |
| System containing <i>Tubifex</i> sp                                             | X(3)                             | X                     | X                     | X                  |                                             |                       |                       |                    | X(3)                              |                    | X(3)                                         |                    |
| System containing <i>Chironomus</i> sp and <i>Tubifex</i> sp                    | X(3)                             | X                     | X                     | X                  |                                             |                       |                       |                    | X(2)                              |                    | X                                            |                    |
| System containing <i>Chironomus</i> sp, <i>Tubifex</i> sp and <i>Valvata</i> sp |                                  |                       |                       |                    |                                             |                       |                       |                    | X(2)                              | X                  | X                                            | X                  |
| Anaerobic conditions                                                            | X(3)                             | X                     | X                     |                    |                                             |                       |                       |                    | X(2)                              |                    |                                              |                    |
| Fixed conditions                                                                | X(3)                             | X                     | X                     |                    |                                             |                       |                       |                    |                                   |                    | X(2)                                         |                    |
| No organisms added                                                              | X                                | X                     | X                     |                    | X                                           | X                     | X                     | X                  | X                                 | X                  | X                                            | X                  |

of Clophen A 50 than undisturbed cores because of their larger sediment volumes.

The amount of added substances was kept low to correspond to natural conditions, eg sediment contaminated with PCBs. This precaution is essential to acquire ecologically useful information. Furthermore, the added substances were not to have acute toxic effects on organisms in the sediment.

### Analytical methods

Material from jet drops collected on the impactor tape was extracted with hexane. After concentration by evaporation, the extract was analyzed by gas chromatography (21). The microlayer was analyzed according to Larsson *et al* (19). Water, sediment and organisms were extracted, cleaned-up, and analyzed by gas chromatography (22). The minimum detectable quantity was 45 pg for individual PCB compounds and 0.2 ng for Clophen A 50.

### RESULTS

The level of PCBs in sediment from Lake Havgårdssjön was low and represents the "background" level of PCBs in unpolluted lake sediment in the area (Table 3). No PCBs were detected in the lake water.

Both at 5°C and at 18°C the activity of macroorganisms resulted in an increase in suspended material in the water compared to systems without animals. The fixed sys-

tems remained clear, and no changes occurred during the study period. Gas developed in the sediment incubated under anaerobic conditions and caused a release of particles and interstitial water to the overlying water.

Although PCBs were injected below the sediment surface, there was a transport to the overlying water in the systems containing macroorganisms and in the anaerobic systems (Table 4).

The amount of PCBs detected in the water was dependent upon the presence of particles. That PCBs were attached to particles was shown by the small amounts found in centrifuged water samples (Table 5).

PCBs were taken up from the sediment and accumulated in the macroorganisms (Table 6). At the end of the experiment the amount of PCBs in chironomids was several times that found in the sediment.

**Table 5.** PCBs (ng/l) in the water of laboratory model ecosystems incubated under aerobic and anaerobic conditions at 5°C. Sieved sediment was used as bottom substrate. The water was analyzed without removal of suspended particles (water + seston) or after centrifugation at 3000 rpm (water). n.d. = not detected, n.a. = not analyzed.

| System                                                                      | Clophen A 50 | Tetrachlorobiphenyl | Pentachlorobiphenyl |
|-----------------------------------------------------------------------------|--------------|---------------------|---------------------|
| System containing <i>Chironomus</i> sp and <i>Tubifex</i> sp water + seston | 340<br>20    | 300<br>n.a.         | 510<br>12           |
| System containing no animals (AEROBIC) water + seston                       | n.d.<br>n.d. | n.d.<br>n.d.        | n.d.<br>n.a.        |
| System containing no animals (ANAEROBIC) water + seston                     | 340<br>20    | 410<br>n.d.         | 810<br>n.d.         |

**Table 6.** Distribution of PCBs (ng/g, wet weight) in laboratory model ecosystems. Sieved sediment was used as bottom substrate, and the systems were incubated at 5°C and 18°C, respectively. n.a. = not analyzed.

|                                                                                          | Incubated at 5°C |                     |                     | Incubated at 18°C |
|------------------------------------------------------------------------------------------|------------------|---------------------|---------------------|-------------------|
|                                                                                          | Clophen A 50     | Tetrachlorobiphenyl | Pentachlorobiphenyl | Clophen A 50      |
| Sediment                                                                                 | 255              | 98                  | 88                  | 76                |
| <i>Chironomus</i> sp                                                                     | 930              | 435                 | n.a.                | n.a.              |
| <i>Tubifex</i> sp                                                                        | 720              | 615                 | 829                 | 169               |
| <i>Chironomus</i> sp and <i>Tubifex</i> sp (composite sample)                            | 2095             | 2455                | 1010                | 307               |
| <i>Chironomus</i> sp<br><i>Tubifex</i> sp and<br><i>Valvata</i> sp<br>(composite sample) |                  |                     |                     | 167               |

**Table 3.** PCBs in sediment from Lake Havgårdssjön. n.d. = not detected.

| Sediment depth (cm) | PCB (ng/g, dry weight) |
|---------------------|------------------------|
| 0-2                 | 16                     |
| 2-4                 | 8                      |
| 4-6                 | n.d.                   |
| 6-8                 | n.d.                   |
| 8-10                | n.d.                   |

**Table 4.** PCBs (ng/l) in the water of laboratory model ecosystems. Suspended particles were not separated from the water prior to analysis. n.d. = not detected.

| Treatment                                                                       | Sieved sediment incubated at 5°C |                       |                       |                    | Undisturbed sediment cores incubated at 5°C |                       |                       |                    | Sieved sediment incubated at 18°C |                    | Undisturbed sediment cores incubated at 18°C |                    |
|---------------------------------------------------------------------------------|----------------------------------|-----------------------|-----------------------|--------------------|---------------------------------------------|-----------------------|-----------------------|--------------------|-----------------------------------|--------------------|----------------------------------------------|--------------------|
|                                                                                 | Clophen A 50                     | Tetra-chloro-biphenyl | Penta-chloro-biphenyl | No substance added | Clophen A 50                                | Tetra-chloro-biphenyl | Penta-chloro-biphenyl | No substance added | Clophen A 50                      | No substance added | Clophen A 50                                 | No substance added |
| System                                                                          |                                  |                       |                       |                    |                                             |                       |                       |                    |                                   |                    |                                              |                    |
| System containing <i>Chironomus</i> sp                                          | 50                               | 90                    | 85                    | n.d.               | 25                                          | 85                    | 10                    | n.d.               | 4                                 |                    | 4                                            |                    |
| System containing <i>Tubifex</i> sp                                             | 10                               | n.d.                  | 55                    | n.d.               |                                             |                       |                       |                    | 5                                 |                    | 6                                            |                    |
| System containing <i>Chironomus</i> sp and <i>Tubifex</i> sp                    | 340                              | 420                   | 180                   | n.d.               |                                             |                       |                       |                    | 10                                |                    | 8                                            |                    |
| System containing <i>Chironomus</i> sp, <i>Tubifex</i> sp and <i>Valvata</i> sp |                                  |                       |                       |                    |                                             |                       |                       |                    | 6                                 | n.d.               | 11                                           | n.d.               |
| Anaerobic conditions                                                            | 450                              | 310                   | 620                   |                    |                                             |                       |                       |                    | 4                                 |                    |                                              |                    |
| Fixed conditions                                                                | n.d.                             | n.d.                  | n.d.                  |                    |                                             |                       |                       |                    |                                   |                    | n.d.                                         |                    |
| No organisms added                                                              | n.d.                             | n.d.                  | n.d.                  |                    | n.d.                                        | n.d.                  | n.d.                  | n.d.               | n.d.                              | n.d.               | n.d.                                         | n.d.               |

When chironomids and tubificids were incubated together the accumulation was even more pronounced.

In all but the fixed systems, PCBs left the water by jet drops and were recovered 7 cm above the surface of the water (Table 7, 8, Figure 2). The amount varied considerably depending on experimental conditions. The lowest amounts were recorded in undisturbed sediment cores.

PCBs were found in the surface microlayers (Table 7, 8 and Figure 3). Probably

as a result of attachment of particles to the sampling plate, the highest levels of PCBs were found in the microlayer of very turbid, anaerobic systems.

In the three-year old, fixed sediment/water system no PCBs were detected in the surface microlayer or in the water.

In undisturbed cores with macroorganisms incubated at 18°C PCBs moved from the injection sites towards the sediment surface (Table 8). PCBs in the microlayer ranged from 27 ng/dm<sup>2</sup> to 134 ng/dm<sup>2</sup>.

Figure 2. Clophen A 50 on jet drop impactors 7 cm above the water surface of laboratory model ecosystems comprised of sediment, water and macroorganisms.

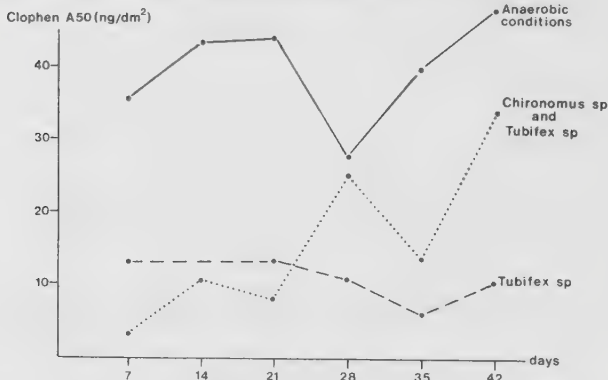


Figure 3. Clophen A 50 in surface microlayers of sediment/water systems to which macroorganisms were added or that were made anaerobic.

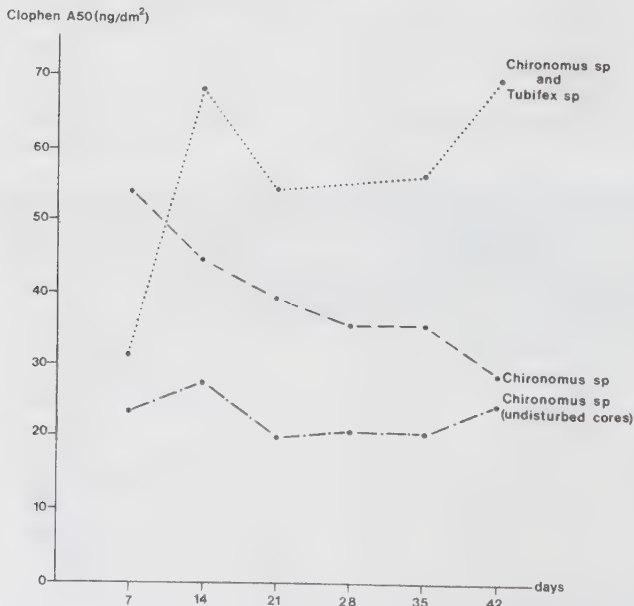


Table 7. Distribution of Clophen A 50 in model ecosystems after incubation for eight weeks at 18°C. Undisturbed sediment cores were used as bottom substrate. n.d. = not detected, n.a. = not analyzed.

| System                                                                          | Clophen A 50 (ng/dm <sup>2</sup> ) |                  |
|---------------------------------------------------------------------------------|------------------------------------|------------------|
|                                                                                 | Surface microlayer                 | Jetdrop impactor |
| System containing <i>Chironomus</i> sp                                          | 5                                  | n.a.             |
| System containing <i>Tubifex</i> sp                                             | n.d.                               | n.a.             |
| System containing <i>Chironomus</i> sp and <i>Tubifex</i> sp                    | 39                                 | n.a.             |
| System containing <i>Chironomus</i> sp, <i>Tubifex</i> sp and <i>Valvata</i> sp | 11                                 | n.a.             |
| No organisms                                                                    | 5                                  | n.a.             |
| Anaerobic conditions                                                            | 87                                 | 42               |

## DISCUSSION

It was expected that PCB compounds would be taken up and accumulated by the macroorganisms. It was not expected, however, that the animals would act as transfer agents for PCBs by their feeding and burrowing activity or by changing the physical and chemical conditions in the sediment. Both chironomids and tubificids increased the amount of suspended particles in the water, thus releasing deposited PCBs from the sediment. Release was even greater when both groups were held together. This effect might be the result of a stress situation induced by crowding, which increases locomotor activity of the organisms. However, it may also indicate synergistic effects: tubificids burrowing deeper channels than chironomids (10, 11) which results in a transport of PCBs from deeper areas to the surface sediment layer. In the surface sediment the PCB compounds are further treated by chironomids.

In addition to effects caused by the movements of the organisms in the sediment, there may be other mechanisms operating that result in a release of PCBs to the water.

Hamenlink *et al* (23), Haque *et al* (24), and Dexter and Pavlou (25) have shown that PCB compounds are readily adsorbed to suspended solids, especially those high in organic carbon. Thus, if the organic composition of the sediment is changed, its capacity to sorb and retain PCBs is also changed. Bioturbation may stimulate bacterial decomposition of organic material in the sediment that results in changed organic composition and, consequently, affects partitioning of PCB compounds between sediment and water.

In undisturbed sediment cores incubated at 18°C, Clophen A 50 moved towards the sediment surface. The transport was probably a result of burrowing activity by the organisms. Depending on the activity of macroorganisms in the sediment, persistent substances may thus be brought to the uppermost sediment layers. The results



Table 8. Clophen A 50 in laboratory model ecosystems incubated under aerobic and anaerobic conditions at 18°C for 8 weeks. Sieved sediment was used as bottom substrate. n.d. = not detected, n.a. = not analyzed.

| System                                                                                   | 0-5 mm | Sediment<br>5-40 mm<br>(ng/g wet<br>weight) | 40-150 mm | Water<br>(ng/l) | Surface<br>micro-<br>layer<br>(ng/dm <sup>2</sup> ) | Jetdrop<br>impactor<br>(ng/dm <sup>2</sup> ) | Organisms<br>(ng/g wet<br>weight) |
|------------------------------------------------------------------------------------------|--------|---------------------------------------------|-----------|-----------------|-----------------------------------------------------|----------------------------------------------|-----------------------------------|
| System containing<br><i>Chironomus</i> sp                                                | 123    | 13                                          | n.a.      | n.d.            | 92                                                  | 16                                           | 106                               |
| System containing<br><i>Chironomus</i> sp                                                | 131    | 18                                          | 7         | 5               | 134                                                 | 15                                           | 106                               |
| System containing<br><i>Tubifex</i> sp                                                   | 31     | 39                                          | 15        | 10              | 93                                                  | 19                                           | 34                                |
| System containing<br><i>Tubifex</i> sp                                                   | 28     | 31                                          | 20        | n.d.            | 114                                                 | 23                                           | 215                               |
| System containing<br><i>Tubifex</i> sp                                                   | 72     | 40                                          | 53        | 6               | 27                                                  | 20                                           | 131                               |
| System containing<br><i>Chironomus</i> sp and<br><i>Tubifex</i> sp                       | 37     | 25                                          | 6         | 6               | 76                                                  | 8                                            | 57                                |
| System containing<br><i>Chironomus</i> sp,<br><i>Tubifex</i> sp and<br><i>Valvata</i> sp | 58     | 46                                          | 19        | 11              | 74                                                  | 13                                           | 74                                |
| Fixed conditions                                                                         | 56     | 657                                         | n.d.      | n.d.            | n.d.                                                | n.d.                                         |                                   |
| No organisms                                                                             | 145    | 440                                         | 142       | n.d.            | n.d.                                                | n.d.                                         |                                   |

show that even if PCB compounds are adsorbed to sedimented particles, there are biological mechanisms which release these compounds to the overlying water, resulting in a recirculation in the aquatic food web. Weiniger (15) stated that PCB compounds accumulated by trout in Lake Michigan were recirculated from the sediment.

In systems without macroorganisms and in fixed systems, PCBs added to the sediment were not relocated, but were recovered in the sediment at the end of the experiment. This underlines the high capacity of sediment to sorb and retain PCB compounds and the importance of bottom-living organisms in releasing such compounds from the sediment.

Anaerobic conditions resulted in a transport of PCBs from the sediment to the water and to the air. Obviously this transport was a result of gas produced in the sediment. Gas production may change chemical and physical conditions within the sediment (26,5). Gas bubbles rising in the water column may also adsorb particles or hydrophobic compounds from the sediment and the water and transfer this material to the surface microlayer. From the microlayer, part of the material will be ejected by jet drops to the air.

The amount of Clophen A 50 added and depth of injection in the sediment were different in the systems incubated at 5°C and 18°C. Compared to systems at 18°C, about four times more Clophen A 50 was added to systems incubated at 5°C. Furthermore, it was injected in the upper 5 mm sediment layer compared with an injection point 20 mm below the sediment surface in the systems incubated at the higher temperature. The substances were deposited at different depths to study transport mechanisms; different incubation temperatures were employed to reveal signs of degradation.

Compared to systems incubated at 18°C, a higher level of PCBs was found in the water, animals, surface microlayer and jet drops of systems incubated at 5°C. However, regarding the burrowing activities of the organisms added, surprisingly low amounts of PCBs were released to the water when the compounds were injected at a depth of 20 mm. This is probably a result of the low amounts injected at that depth. In addition, at 5 mm depths the sediment is not as consistent as at 20 mm; a direct release via interstitial water and particles is therefore more likely when PCBs are injected in the surficial sediment layer.

The PCB mixture and the tetra- and pentachlorobiphenyl behaved in similar ways in the systems. They were accumulated by the macroorganisms and recirculated within the systems. Comparison of the composition of the added PCB mixture to that recovered from sediment and animals showed that no degradation had occurred. This was also the case for the low chlorinated compounds.

Bacteria and microorganisms may leave the aquatic environment by jet drops (16). Certain heavy metals are also attached to jet drop particles, while very little is known about the fate of organic materials. That lipophilic pollutants like PCBs, DDT and related organochlorine residues accumulate in surface films was shown by Duce (18) and Larsson (19). This study indicates that not only are PCBs accumulated in the surface microlayer, but there is also a flux of the compounds from the water to the air. This transport is probably enhanced by the surface microlayer and the bubbles bursting in that layer. However, the results do not permit a conclusion as to whether gas bubbles adsorb PCBs while moving through the water column or upon contact with the microlayer.

If the findings of this study are applicable to conditions in the field, an addi-

tional pathway in the recirculation of PCBs in the environment has to be considered.

Data from actual measurements of PCBs in freshwater and marine sediments are scattered and do not allow estimations of total loads. However, Beeton et al (27) concluded that the Great Lakes sediment represented the greatest PCB reservoir in the continental United States. Kihlström and Berglund (28) suggested, among other alternatives, that large amounts of PCBs may be stored in sediment of the Baltic Sea. Thus, if only a part of the PCBs deposited in these sediments is recirculated, long-term pollution problems may result with the sediment acting as a source of PCBs rather than a sink.

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- See Thorbjörnsen Svensson for skillful technical assistance. The work was supported by the National Swedish Environment Protection Board.
- This manuscript was submitted to *Ambio* September 8, 1980 and accepted for publication November 27, 1980.





## TRANSPORT OF $^{14}\text{C}$ -LABELLED PCB COMPOUNDS FROM SEDIMENT TO WATER AND FROM WATER TO AIR IN LABORATORY MODEL SYSTEMS

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**Abstract**—Tetra-, hexa- and octachlorobiphenyls were added to aquatic model systems composed of undisturbed sediment cores with an overlying water phase. Using impactor plates transport of the compounds from sediment to air was observed. About one per cent of the sediment-bound PCBs recovered in the systems left the water by jet drops from bursting bubbles. The transport of PCBs from the sediment to the air was nearly constant over time, with a transport rate of  $0.62 \mu\text{g} \cdot \text{dm}^{-2} \cdot \text{week}^{-1}$  for tetrachlorobiphenyl. Tetrachlorobiphenyl was mobile in systems with and without macroinvertebrates and in those fixed with  $\text{HgCl}_2$ . Hexa- and octachlorobiphenyls were transported from sediment to water mainly by bioturbation processes. The two latter substances had a higher adsorption to particles than tetrachlorobiphenyl. Compared to tetrachlorobiphenyl, more hexa- and octachlorobiphenyls accumulated in chironomids and tubificids.

**Key words**—PCB, polychlorinated biphenyl, model system, jetdrop, surface microlayer

### INTRODUCTION

Transport of PCBs (polychlorinated biphenyls) to various organisms in aquatic food webs has been extensively studied (Jensen *et al.*, 1969; Holden, 1972; Risebrough and deLappe, 1972). However, the transport of man-made pollutants between different abiotic compartments of the ecosystem is not as well known. This is especially true for the flux of PCBs to the sediment via sedimenting materials, its redistribution within the sediment and its release from the sediment to the water.

PCBs that settle to the bottom of lakes and watercourses are partly incorporated into the sediment and partly redistributed to the water. Mechanisms that control the transport from sediment to water are desorption (Halter and Johnson, 1977; Wildish *et al.*, 1980), bioturbation, gas convection (Södergren and Larsson, 1982) and erosion (Olsson *et al.*, 1978). Also, via benthic organisms PCBs may directly be taken up from the sediment to the food chain. It has been shown (Nimmo *et al.*, 1971; Courtney and Langston, 1978; Elder *et al.*, 1979) that invertebrates living in PCB-contaminated bottom areas accumulate PCBs directly from the sediment.

Both chemical and biological mechanisms may thus activate PCBs settled into the sediment of lakes and oceans. From the water lipophilic pollutants like PCBs may further be transported and enriched in the surface microlayer (Duce *et al.*, 1972; Larsson *et al.*, 1974) or transported to the air (Blanchard and Syzdek, 1972; Southworth, 1979; Chiou, 1980). Mechanisms that may govern the transport are jet drops (Södergren and Larsson, 1982), evaporation (Southworth, 1979) and co-distillation (Bowman *et*

*al.*, 1964). The effectiveness of removing PCBs from the waterphase to the air by bubbles was demonstrated by Colenutt and Thorburn (1980). A transport of PCBs from sediment to air has been shown to occur in aquatic model systems by Södergren and Larsson (1982).

Commercial PCB mixtures consist of about 100 individual PCB compounds (Widmark, 1968; Hutzinger *et al.*, 1974). The compounds behave differently in the ecosystem, owing to their various chemical and physical properties. Highly chlorinated compounds have a more lipophilic character and consequently a lower water solubility, they also have higher adsorption to various surfaces and show more pronounced accumulation in biota than lower chlorinated PCBs (Hutzinger *et al.*, 1974; Haque *et al.*, 1974). Lower chlorinated biphenyls in commercial PCB mixtures seems to be more easily desorbed from sediment to water than the highly chlorinated ones (Halter and Johnson, 1977) and have a higher evaporation rate (Hutzinger *et al.*, 1974).

To study transport mechanisms of individual PCB compounds, with different chemical and physical properties (Hutzinger *et al.*, 1974), tetra-, hexa- and octachlorobiphenyls were added to aquatic model systems composed of undisturbed sediment cores with an overlying water phase. To some systems benthic macroinvertebrates were added, some were without animals, others were fixed with  $\text{HgCl}_2$ , or made anaerobic. The transport rates of the individual PCB compounds from sediment to air via jet drops from bursting bubbles were followed by collecting the drops on a Teflon impactor 7 cm above the surface of the water.

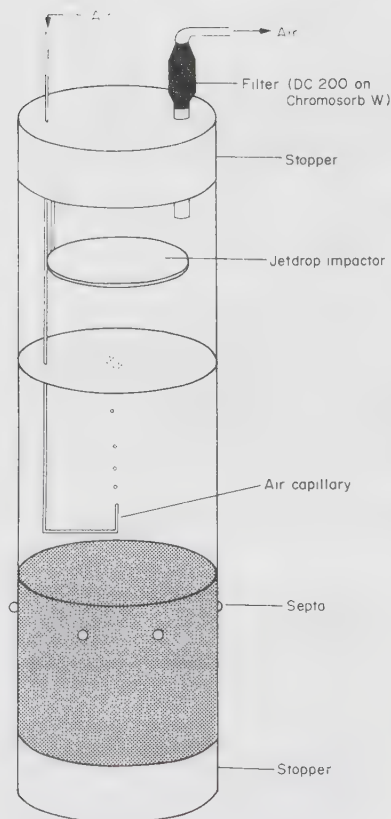


Fig. 1. Experimental set-up to study movement of PCBs to the water and air from undisturbed sediment cores.

## MATERIALS AND METHODS

### Model components

Undisturbed sediment cores with an overlying water phase were taken with a Kajak-type corer. The cores were collected in Lake Havgårdssjön, situated in south Sweden. The location of the lake and the water/sediment data are described elsewhere (Södergren and Larsson, 1982). Chironomids (*Chironomus plumosus*-type) were collected in the nearby Vombsjön and tubificids (*Tubifex tubifex*) were cultured in the laboratory.

### Model systems

The experiment was carried out at 5°C in the dark. The model systems consisted of tubes sealed with rubber stop-

pers (Fig. 1). To minimize the binding of lipophilic substances to the walls and allow as complete removal of adsorbed substances as possible, the tubes were made of glass. The systems were composed of 500 g undisturbed sediment and 600 g water. Thirty chironomids (7500 individuals  $m^{-2}$ ) and about 100 tubificids (25,000 individuals  $m^{-2}$ ) were added to systems in which bioturbation was studied (Table 1). Some systems were fixed by adding 5 ml 5%  $HgCl_2$  to the water, while others were made anaerobic by continuously bubbling the water phase with nitrogen gas. In the aerobic systems the water was bubbled with air (1–2 bubbles  $s^{-1}$ , 1–3 mm in diameter) from a metal capillary tube located 5 cm over the sediment surface. The same procedures were followed in the anaerobic systems except that the water were bubbled with nitrogen gas. Before leaving the systems, the air and nitrogen passed a filter consisting of diatomaceous material (Chromosorb W, 200 mesh) impregnated with a silicon oil (DC 200, 5%). The filters collect lipophilic substances leaving the systems via the air or the nitrogen gas.

Transport of added compounds from the water to the air by jet drops was followed by collecting the drops on a Teflon impactor 7 cm above the surface of the water. The impactor plates were sampled weekly; at the same time the surface microlayers was collected according to Södergren (1979).

After 10 weeks the experiment was terminated. The water of the systems was drawn off with a glass siphon, carefully not to disturb the sediment surface. After centrifugation of the water at 2000 g, one particle and one water fraction were obtained. Particles that were attached to the glass-walls above the sediment surface of the systems were removed and their content of PCB compounds determined separately.

Sediment samples were taken at three different levels below the sediment surface: 0–5, 5–30 and 30–110 mm. The sediment from each level was mixed, and subsamples of 20 g (the macroinvertebrates removed) were analyzed. The remaining sediment was sieved and the macroinvertebrates were collected. After washing the stoppers and walls of the systems with distilled water, PCBs still adsorbed were extracted with acetone/hexane, 1:1.

### Studied substances

$^{14}C$ -labelled substances were used in the experiment. 585  $\mu g$  2,2',4,4'-tetrachlorobiphenyl (sp. act.  $17.7 \times 10^3$  MBq  $mol^{-1}$ ), 561  $\mu g$  2,2',4,4',5,5'-hexachlorobiphenyl (sp. act.  $23.6 \times 10^3$  MBq  $mol^{-1}$ ) and 531  $\mu g$  2,2',3,3',4,4',5,6'-octachlorobiphenyl (sp. act.  $28.6 \times 10^3$  MBq  $mol^{-1}$ ) were added to each system respectively (Table 1). The substances were dissolved in 100  $\mu l$  acetone and injected through silicon septa at six different places in the walls of the tubes 10 mm below the sediment surface (Fig. 1). This technique enables an addition of PCBs without disturbing the sediment surface or contaminating the water phase. PCBs were added to the sediment to an overall concentration of about 1 ppm (wet wt).

### Extraction and analysis

Sediment, water and macroinvertebrates were treated according to Södergren (1973). Particles that were separated from the water by centrifugation, and particles adhered to the walls of the model systems were extracted with a mixture of 8 ml of acetone/hexane (1:1). The extracts were then ultrasonic treated for 10 min. The glass-walls of the systems

Table 1. Experimental set-up, substances added and treatment of the model systems

| Treatment                   | Substance | 2,2',4,5'-<br>Tetrachlorobiphenyl | 2,2',4,4',5,5'-<br>Hexachlorobiphenyl | 2,2',3,3',4,4',5,6'-<br>Octachlorobiphenyl |
|-----------------------------|-----------|-----------------------------------|---------------------------------------|--------------------------------------------|
| Macroinvertebrates added    |           | 3 Systems                         | 3 Systems                             | 3 Systems                                  |
| No macroinvertebrates added |           | 1 System                          | 1 System                              | 1 System                                   |
| Fixed with $HgCl_2$         |           | 1 System                          | 1 System                              | 1 System                                   |
| Anaerobic                   |           | 1 System                          | 1 System                              | 1 System                                   |

Table 2. Distribution and recovery of PCBs in sediment of the systems

| Substance added<br>Treatment of<br>Systems | Tetrachlorobiphenyl<br>( $\mu\text{g g}^{-1}$ , fresh weight) |                             |       |           | Hexachlorobiphenyl<br>( $\mu\text{g g}^{-1}$ , fresh weight) |                             |       |           | Octachlorobiphenyl<br>( $\mu\text{g g}^{-1}$ , fresh weight) |                             |       |           |
|--------------------------------------------|---------------------------------------------------------------|-----------------------------|-------|-----------|--------------------------------------------------------------|-----------------------------|-------|-----------|--------------------------------------------------------------|-----------------------------|-------|-----------|
|                                            | Macroinvertebrates added                                      | No macroinvertebrates added | Fixed | Anaerobic | Macroinvertebrates added                                     | No macroinvertebrates added | Fixed | Anaerobic | Macroinvertebrates added                                     | No macroinvertebrates added | Fixed | Anaerobic |
| Sediment Level                             |                                                               |                             |       |           |                                                              |                             |       |           |                                                              |                             |       |           |
| 0-5 mm                                     | 3.9                                                           | 15.8                        | 5.5   | 10.5      | 3.0                                                          | 4.0                         | 2.9   | 5.2       | 3.0                                                          | 2.0                         | 7.0   | 8.2       |
| 5-30 mm                                    | 2.2                                                           | 1.1                         | 5.2   | 0.2       | 2.1                                                          | <0.1                        | 1.0   | 0.4       | 1.1                                                          | 0.3                         | 0.3   | 0.2       |
| 30-110 mm                                  | <0.1                                                          | ND                          | <0.1  | ND        | 0.1                                                          | ND                          | 0.1   | ND        | <0.1                                                         | <0.1                        | <0.1  | <0.1      |
| Total amount in sediment                   | 314.3                                                         | 401.9                       | 797.2 | 208.4     | 296.6                                                        | 119.9                       | 173.3 | 155.0     | 213.9                                                        | 88.1                        | 183.7 | 152.0     |
| % of recovered PCBs in the systems         | 97.7                                                          | 98.3                        | 99.8  | 99.3      | 96.1                                                         | 99.9                        | 98.9  | 99.9      | 90.0                                                         | 99.6                        | 99.8  | 99.4      |
| ND: Not detected.                          |                                                               |                             |       |           |                                                              |                             |       |           |                                                              |                             |       |           |

were washed with  $2 \times 20$  ml of acetone/hexane (1:1), and stoppers and filters were extracted with  $2 \times 5$  ml acetone/hexane (1:1). Jet drop impactors were extracted with  $2 \times 5$  ml acetone/hexane (1:1) in an ultrasonic bath for 10 min. Surface microlayers were analyzed according to Larsson *et al.* (1974).

The extracts were evaporated under a gentle stream of nitrogen gas to 0.1 ml. A 20 ml aliquot of Insta Fluor 2 was added and the radioactivity determined on a Tri-Carb 460-CD liquid scintillator (Packard). The limit of detection was about 4 ng for the chlorobiphenyls. At regular intervals samples were taken for gas chromatographic analysis (Södergren and Larsson, 1982).

## RESULTS

### Mass balance

A mass balance of the added compounds within the model systems shows that on average 68% of the tetrachlorobiphenyl was recovered. 40 and 31% were recovered of hexa- and octachlorobiphenyls respectively.

Most of the PCBs added was found in the sediment. The largest amounts of PCBs were always deposited in the surficial sediment layer (Table 2). Below 30 mm sediment depth, no or only minor amounts, were found.

A higher mobility of PCB compounds within the systems was observed when macroinvertebrates were present (Fig. 2). This was partly due to uptake in the organisms (1-3% of recovered PCBs) but also to the activity of the macroinvertebrates that resulted in a transport of PCBs to different compartments of the systems. The bioturbation effect caused a transport of particles from the sediment to the water. Most of these particles adhered to the walls of the glass tubes, and contained about 5.0% of the recovered octachlorobiphenyl, 0.5% of hexachlorobiphenyl and 0.2% of the tetrachlorobiphenyl (Fig. 2). Particles present in the water (siston) of the macroinvertebrate systems contained 1.01% of the octachlorobiphenyl, 0.14% of hexachlorobiphenyl and 0.07% of the tetrachlorobiphenyl. In systems with no macroinvertebrates PCBs on particles attached to the glass walls and PCBs in seston were of minor importance. Recovery of PCBs dissolved in the water of the systems ranged from 0.01 to 0.09%. However, in the anaerobic system with octachlorobiphenyl added, a greater amount (0.42%) was found in the water.

In systems containing macroinvertebrates 0.4-1.0% of recovered PCBs left the water via jet drops from bursting bubbles and were retrieved by the impactor plates. However, even if no macroinvertebrates were present, the transport occurred for tetrachlorobiphenyl (1.5% of recovered tetrachlorobiphenyl).

### Uptake in organisms

Hexa- and octachlorobiphenyls were accumulated to a larger extent than tetrachlorobiphenyl by the macroinvertebrates (Fig. 3). A comparison among the species shows that chironomids accumulate PCBs

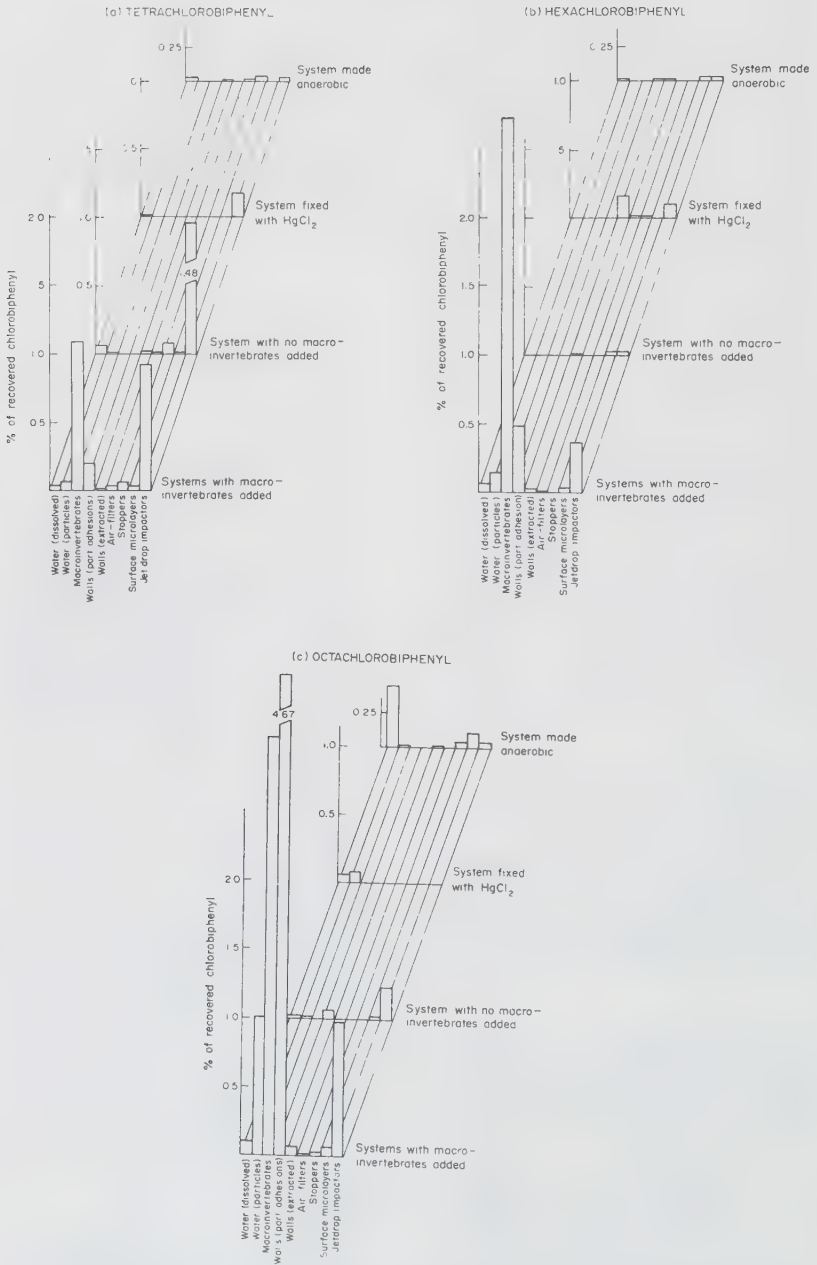


Fig. 2. Distribution of recovered PCBs in different compartments of the systems. X-axis—treatment of the systems, Y-axis—percent of recovered PCBs; Z-axis—the different compartments of the systems.



# Transport of $^{14}\text{C}$ -labelled PCB compounds

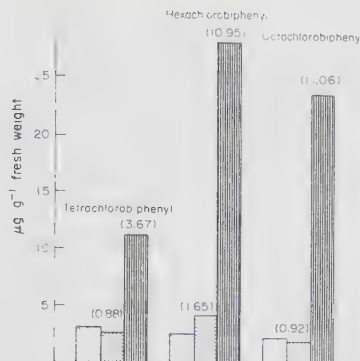


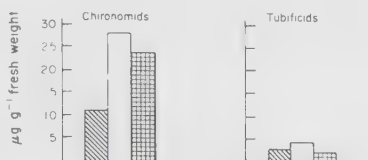
Fig. 3. Levels of PCBs in macroinvertebrates in relation to the concentration in sediment (0–30 mm). Figures within brackets refer to accumulation factors: ( $\mu\text{g PCB g}^{-1}$  wet weight of animals)/( $\mu\text{g PCB g}^{-1}$  wet weight of sediment). □—Sediment; ▨—tubificids; ▩—chironomids.

to a higher degree than tubificids (Fig. 4). The accumulation factor on a wet weight basis ( $\mu\text{g PCBs}$  in animals/ $\mu\text{g PCBs}$  in sediment) for tubificids was near unity, while for chironomids the corresponding factor for tetrachlorobiphenyl was about 4 and for hexa- and octachlorobiphenyl near 11 (Fig. 3).

## Transport to water

The added substances were transported from the sediment to the water in all systems that contained

## CALCULATION BASED ON FRESH WEIGHT



## CALCULATION BASED ON FAT WEIGHT

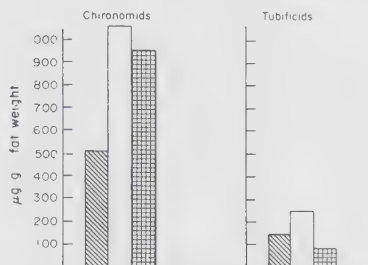


Fig. 4. Levels of PCBs in chironomids and tubificids of the aquatic model systems. ▨—Tetrachlorobiphenyl; □—hexachlorobiphenyl; ▩—octachlorobiphenyl.

macroinvertebrates (Fig. 5). In these systems most PCBs were adsorbed to particles and the adsorption was most pronounced for octachlorobiphenyl. In systems without macroinvertebrates and in systems

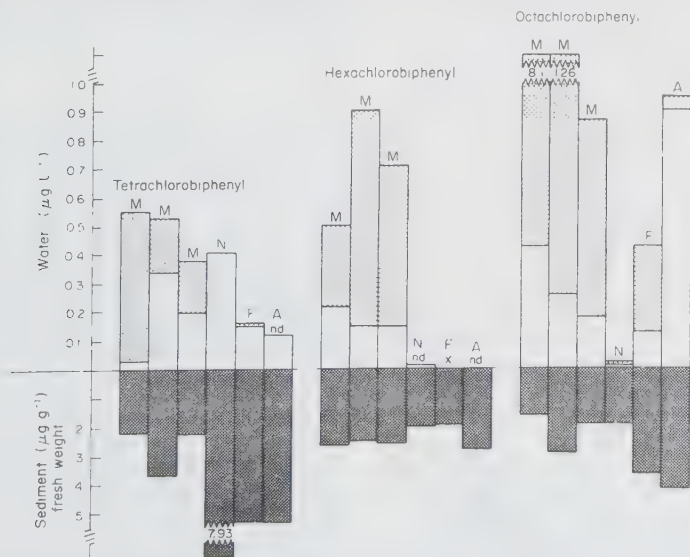


Fig. 5. PCBs in water and sediment of systems with macroinvertebrates (M). Without macroinvertebrates (N), fixed (F) and made anaerobic (A). ▨—PCB adsorbed to particles; □—PCB dissolved in the water; ▩—PCB in the sediment; ×—not analyzed; nd—not detected.

Table 1. PCBs adsorbed to glass-walls, particle adhesions on the glass-walls and to stoppers in the aquaria model systems.

| PCBs adsorbed to<br>Glass walls<br>Particles adhered<br>to glass walls<br>Stoppers | Tetrachlorobiphenyl<br>Systems ( $\mu\text{g}$ ) |                               |                                  | Hexachlorobiphenyl<br>Systems ( $\mu\text{g}$ ) |                               |                                  | Octachlorobiphenyl<br>Systems ( $\mu\text{g}$ ) |                               |                                  |
|------------------------------------------------------------------------------------|--------------------------------------------------|-------------------------------|----------------------------------|-------------------------------------------------|-------------------------------|----------------------------------|-------------------------------------------------|-------------------------------|----------------------------------|
|                                                                                    | With<br>macroinvertebrates                       | Without<br>macroinvertebrates | Fixed<br>with<br>$\text{HgCl}_2$ | With<br>macroinvertebrates                      | Without<br>macroinvertebrates | Fixed<br>with<br>$\text{HgCl}_2$ | With<br>macroinvertebrates                      | Without<br>macroinvertebrates | Fixed<br>with<br>$\text{HgCl}_2$ |
|                                                                                    | 0.032<br>0.376<br>0.149                          | 0.065<br>ND<br>0.345          | 0.007<br>ND<br>0.065             | 0.071<br>1.414<br>0.017                         | 0.014<br>0.001<br>ND          | 0.223<br>ND<br>0.025             | 0.146<br>11.170<br>0.041                        | 0.010<br>0.057<br>ND          | 0.010<br>0.009<br>ND             |

ND Not detected



Fig. 6. PCBs in surface microlayers of the systems after 10 weeks.

□—systems with macroinvertebrates;  
 ■—systems without macroinvertebrates; ■—systems fixed with  $\text{HgCl}_2$ ; ▨—systems made anaerobic.

that were fixed only minor amounts were recovered in the water. In the anaerobic system to which octachlorobiphenyl had been added the water contained appreciable amounts ( $0.95 \mu\text{g l}^{-1}$ ), while the opposite was true for anaerobic systems of tetra- and hexachlorobiphenyls. The high levels of octachlorobiphenyl observed may be a result of adsorption to particles small enough not to sediment under centrifugation.

PCBs were adsorbed to the glass walls of the systems and to particles attached to the walls (Table 3). The adsorption to the walls and to the attached particles increased in order tetra- hexa- octa-chlorobiphenyl.

#### Accumulation in the surface microlayer

PCBs were detected in the surface microlayer of all systems. However, the amounts of PCBs in the microlayer were too low to be quantified on a weekly basis. After 10 weeks the largest amounts of PCBs were recorded in the surface microlayers of systems that contained macroinvertebrates (Fig. 6). Among the substances studied, octachlorobiphenyl was enriched in the microlayer of these systems to the highest concentration.

#### Transport by jet drops from bursting microbubbles

The quantities of PCBs trapped by the jetdrop impactors were higher than those of the surface microlayers. The transport rate to the jetdrop impactors was largest for tetrachlorobiphenyl (Fig. 7). Moreover, no major differences in transport rates were observed between systems with and without macroinvertebrates or in fixed systems as regards tetrachlorobiphenyl. The transport rates of hexa- and octachlorobiphenyls to jetdrop impactors were higher in systems containing macroinvertebrates than in systems without macroinvertebrates, in fixed systems or in systems made anaerobic (Figs 7 and 8).

In systems containing macroinvertebrates the transport of PCBs from the sediment to the air show small differences with time (Figs 7 and 9). The transport rate ( $k$ ) for tetrachlorobiphenyl was  $0.62 \mu\text{g dm}^{-2} \text{ week}^{-1}$ . The results of the first week were excluded when calculating the transport rate because of high initial activity of the macroinvertebrates in the sediment.

Only minor amounts of the PCB compounds left the systems with the air (Fig. 10). Again tetra-

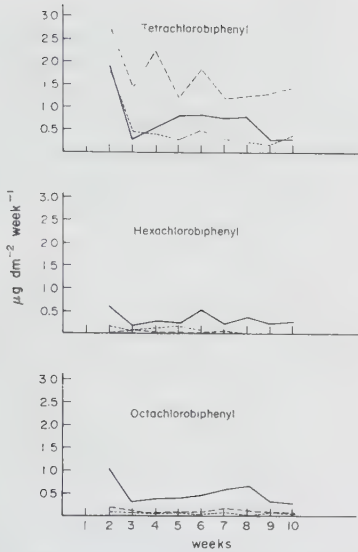


Fig. 7. PCBs collected on jetdrop impactors in the aquatic model systems. (—) Systems with macroinvertebrates; (---) systems without macroinvertebrates; (....) systems fixed with  $\text{HgCl}_2$ .

chlorobiphenyl was more mobile than the other PCB compounds. It is evident that the invertebrate organisms are important in the transport processes, as larger amounts left the systems when macroinvertebrates were present.

#### DISCUSSION

A strong adsorption of PCBs to the surficial sediment was expected due to its usual high organic carbon content (Steen *et al.*, 1978). The surficial sediment ought to have more affinity (adsorption sites) for PCBs, thus acting as a barrier for PCB transport from lower sediment levels to the water. The properties of this surficial sediment barrier, compared to lower sediment levels, consist of: (1) a more complex, less broken down, "biologically active" structure, with higher content of lipids, proteins etc; (2) a higher organic content; (3) a less consoli-

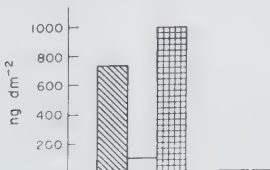


Fig. 8. PCBs on jetdrop impactors in anaerobic model systems after 10 weeks. (▨) —Tetrachlorobiphenyl; (■) —Hexachlorobiphenyl; (■) —octachlorobiphenyl.

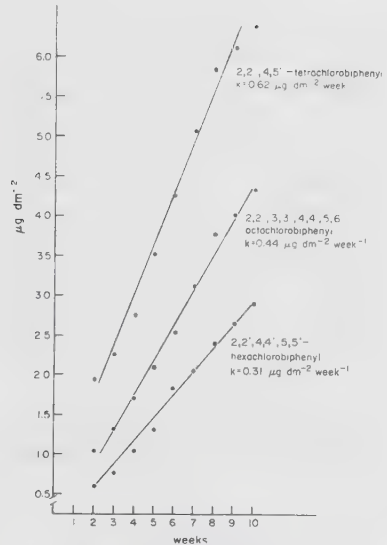


Fig. 9. Accumulated amounts of PCBs on jetdrop impactors in systems with macroinvertebrates added.

dated structure, with larger active surface; (4) a higher content of bacteria. However, a transport from sediment to water occurred, partly mediated by macroinvertebrates.

It is suggested that chironomids and tubificids transfer PCBs to the sediment interface, either in a dissolved form or attached to particles. At the interface, the compounds are exposed to mechanisms that may result in a transport to other compartments in the ecosystem (water, surface microlayer, air etc.) or in incorporation in the food web. The mechanisms

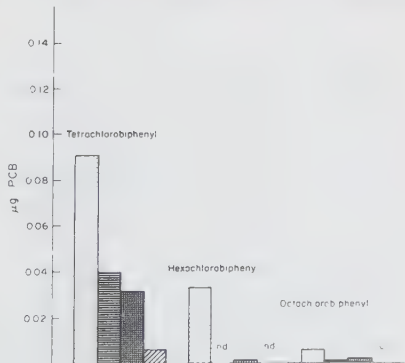


Fig. 10. PCBs trapped on airfilters in different systems. (□) —Systems with macroinvertebrates; (▨) —systems without macroinvertebrates; (■) —systems fixed with  $\text{HgCl}_2$ ; (▤) —systems made anaerobic; nd—not detected.

that may operate in the sediment/water interface include particle transport, dissolution and bubble transport. The bioturbation induced transport over the interface is partly caused by the burrowing activity of the animals, that reactivate PCBs in lower sediment levels, and enables a transport across the barrier of organic surface sediment.

#### Mass balance

The amounts of hexa- and octachlorobiphenyls recovered in the systems were low. This is probably due to the affinity of these compounds to particles and glass-surfaces which prevents effective extraction (Haque *et al.*, 1974; Pepe and Byrne, 1980). 1–3% of the PCBs recovered were found accumulated in macroinvertebrates. Also transport to air, as indicated by jetdrop impactors, were found to be an important compartment of the mobile PCB fraction.

In macroinvertebrate systems to which octachlorobiphenyl was added particle adhesions on the glass walls showed to be a major site for deposition of the compound. That the octachlorobiphenyl to a higher degree was adsorbed to particles, then tetra- and hexachlorobiphenyls, are explained by the more lipophil and adsorptive quality of this compound (Hutzinger *et al.*, 1974; Haque and Schmedding, 1976).

#### Uptake in organisms

Tetrachlorobiphenyl was not taken up by macroinvertebrates to the same extent as hexa- and octachlorobiphenyls. This is probably an effect of the lower number of chlorine atoms in the molecule that gives the compound a less lipophilic character (Hutzinger *et al.*, 1974; Higushi, 1976). However, the tetrachlorobiphenyl might also be more easily degraded by macroinvertebrates than hexa- and octachlorobiphenyls, resulting in lower levels of less chlorinated biphenyls. This has been shown to occur in vertebrates (Yoshimura and Yochihara, 1976; Hutzinger *et al.*, 1974).

The PCB compounds accumulated more in chironomids than in tubificids. As chironomids (*Chironomus plumosus*-type) live in close contact with the surficial sediment (Jónasson, 1972), they were exposed to considerably larger amounts of PCBs in the model systems, as the upper 5 mm of the sediment contained the major part of the PCB compounds. Tubificids, on the other hand, feeding on lower sediment levels (Davis, 1974) that were less contaminated, reduce their exposure to PCBs.

The differences in accumulation may also be a physiological effect (Insecta vs Annelida). For instance, at the end of the larval stage (fourth instar larvae) just before pupating and hatching, chironomids may have an increased metabolism compared to tubificids. A higher feeding rate and consequently, a higher PCB intake/time unite, results in a more rapid uptake of PCBs by chironomids compared to tubificids.

The highest accumulation factors were obtained for chironomids. Consequently, in lakes with large amounts of deposited PCBs in the sediment, food webs where chironomids dominate may get a higher input of PCB compounds compared to food webs dominated by tubificids. Moreover, in late spring an increase of the levels of PCBs is expected in predatory fishes that primarily feed on fourth instar/pupating chironomids [e.g. pope (*Gymnocephalus cernua*) and trout (*Salmo trutta*)].

#### Transport to water

Transport of tetrachlorobiphenyl from sediment to water appears not to be influenced by bioturbation, since the compound was desorbed from sediment in systems that contained no macroinvertebrates or that were fixed. Tetrachlorobiphenyl is the most water soluble of the compounds used, and the results indicate that movement of this compound from sediment to water is governed mainly by desorption processes (Hutzinger *et al.*, 1974; Halter and Johnson, 1977).

The association of PCBs to particles increases in order tetra-, hexa- and octachlorobiphenyl (Haque and Schmedding, 1976). As macroinvertebrate activity results in generation of particles to the water, contaminated sediment particles are transferred to the overlying water column. Thus, larger number of macroinvertebrates in the sediment will increase transport of particles and, consequently result in a larger flow of persistent chlorinated compounds from sediment to water. In the model systems bioturbation processes moved hexa- and octachlorobiphenyls deposited in the sediment to the water via particles, that either remained in solution (seston) or were adsorbed to the glass walls.

In lakes and watercourses bioturbation processes could mean an increased availability of sediment-bound PCBs entering aquatic food chains, starting with particle feeders. Bioturbation could also increase the mobility of PCB compounds transported to other parts of the ecosystem.

#### Accumulation in the surface microlayer

A high enrichment of PCBs was noted in the surface microlayers of systems that contained macroinvertebrates. Furthermore, the amount of PCBs in the microlayer was related to the PCB concentration in the subsurface water; a high enrichment in the microlayer was found when the concentration of PCBs in the water was high, as has been observed for other substances (Hunter and Liss, 1977).

Among the substances studied octachlorobiphenyl showed the highest enrichment in the microlayers. As particles are more abundant in marine (Sieburth *et al.*, 1976) and freshwater microlayers (Södergren, in preparation) compared to subsurface water, it is assumed that octachlorobiphenyl adsorbed to particles are trapped in the microlayer of the model

systems. Octachlorobiphenyl has a higher affinity to particles than tetra- and hexachlorobiphenyls.

#### *Transport by jet drops from bursting microbubbles*

Among the studied compounds, tetrachlorobiphenyl had the highest rate of transport to the impactor plates (and presumably to the air) by jet drops from bursting bubbles. The movement of tetrachlorobiphenyl from sediment to air is regulated by at least two mechanisms: (1) A desorption from sediment to water, that results in higher amounts in the water of the more water soluble tetrachlorobiphenyl compared to hexa- and octachlorobiphenyls. (2) Tetrachlorobiphenyl is adsorbed to the microbubbles rising through the water column, and is transported to the jetdrop impactors when the bubbles burst in the surface microlayer. The higher concentration of the tetrachlorobiphenyl in the water compared to hexa- and octachlorobiphenyls makes the compound more "available" for bubble association (there is a higher probability that a tetrachlorobiphenyl-molecule will adsorb to a rising microbubble). The higher evaporation rate of tetrachlorobiphenyl (Hutzinger *et al.*, 1974) may also play an important role in transport from water to air.

The mobility of tetrachlorobiphenyl in the model systems was also shown by the amounts found in air filters. This compartment may to some extent reflect the aerosol bound PCBs that can be transported over long distances.

Hexa- and octachlorobiphenyls were transported by jet drops primarily in systems that contained macroinvertebrates. Affected by bioturbation processes, the substances are released from the sediment to the water (either in dissolved form or associated to particles), and are trapped by the microbubbles. In systems without macroinvertebrates or in systems that were fixed the extent of transport to the impactor plates was low. The results indicate that the flux of hexa- and octachlorobiphenyls from sediment to water to air is mainly dependent on bioturbation processes, while tetrachlorobiphenyl seems to be more mobile and its transport governed mainly by desorption.

Compared to aerobic systems the mobility of PCBs in anaerobic systems was low. One of the processes that may regulate transport of PCBs in anaerobic systems is production of gas in the sediment. Once the gas is released from the sediment, bubbles are formed that will collect particles and PCBs (Södergren and Larsson, 1982). However, production of gas in the sediment was not observed. This was probably due to insufficient amounts of organic matter in the sediment, that resulted in low substrate amounts for anaerobic bacteria. Therefore, the movement of PCBs in the anaerobic systems was mostly governed by desorption processes.

In systems that contained macroinvertebrates the rate of transport of PCBs from sediment to air (as shown by the PCBs accumulated on jetdrop im-

pactors) showed small differences with time. The constant rate of the PCB transport from sediment to air was probably a result of the stable conditions in the systems.

The rate of transport from sediment to air did not decline during the ten weeks experiment, indicating that the process would continue until the PCB content of the sediment is exhausted. As the amount of PCBs in the sediment is large compared to the amounts in water and air, the process may operate for a long time. PCBs deposited in the sediment may thus increase levels in biota in areas where no or minor other input occurs. Areas with contaminated bottom sediments like the Baltics (Odén and Ekstedt, 1976; Kihlström and Berglund, 1978) and the Great Lakes (Beeton *et al.*, 1979) could thus act as a source for PCBs rather than a sink.

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UPTAKE OF SEDIMENT RELEASED PCBs BY THE EEL  
(*ANGUILLA ANGUILLA*), IN STATIC MODEL SYSTEMS.

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## Abstract

PCBs (Clophen A 50) were added to sediment (1 ug/g fresh weight) of 60 l aquaria that contained sediment, water, benthic macroinvertebrates and eels. To compare uptake of PCBs in eels that fed on macroinvertebrates in the sediment to eels that were separated from the sediment, the bottom of some systems were screened off with a net.

In all systems, except the control, PCBs were transported from the sediment to the water so that a concentration of 0.2-0.7 ug/l was obtained. The transport was dependent on benthic macroinvertebrates and was related to the transfer of particles across the sediment/water interface.

PCBs in eels that were separated from the sediment ranged from 2.5 to 8.9 ug/g fresh weight after 77 days. In eels that were allowed to feed in the sediment the concentration was 7.2-14.1 ug/g.

The results show that PCBs were released from sediment to the water, and were taken up by the eel directly from the water presumably as a result of water/fat partitioning processes in the fishes.

## 1. Introduction

Uptake of PCBs by fish from contaminated sediment has been proposed by several authors (Young et al. 1977, Halter and Johnson 1977, Weininger 1978, Courtney and Langston 1980). The mechanisms of such a transport include desorption of PCBs from sediment to water and uptake from water mainly by the gills of the fishes, and/or an uptake via resuspended particles containing PCBs (by adsorption or exchange processes (Omann and Lakowicz 1981) or ingestion).

The availability of sediment-bound PCBs for fishes depend among other things on their habitat. Bottom-feeding fishes like flounder (Platichthys flesus L.), pope (Gymnocephalus cernua L.) or eel (Anguilla anguilla L.) that live and feed in direct contact with the sediment may be exposed to higher amounts of PCBs than fishes in the open water. For pelagic fishes, however, the availability of PCBs in the sediments depends on the degree of redistribution to the overlying water column. Processes that may act in the redistribution include desorption (Halter and Johnson 1977, Wildish et al. 1980), resuspension of particles from sediment (Olsson et al. 1978, Hargrave 1976, Warry and Chain 1981), altered physical/chemical conditions in the sediment, like pH, salinity, organic content etc. (Pionke and Chesters 1973) and activity of benthic macroinvertebrates in the sediment (Södergren and Larsson 1982).

It has been questioned whether the uptake of organochlorine residues in aquatic animals is governed mainly by accumulation via the food chain (Risebrough and deLappe 1972), or as a partitioning process between water and the fat of the animal (Hamenlink et al. 1971, Chiou et al. 1977, Clayton et al. 1977, Dexter and Pavlou 1979). The more "traditional" biomagnification theory includes, for instance, an uptake by ingestion of residues from sediment by macroinvertebrates (Nimmo et al. 1971) and a further uptake by predators. On the other hand, an uptake of the compound could occur directly from sediment or interstitial water to the invertebrates by a partitioning process

(Fowler et al. 1978, Courtney and Langston 1978, McLeese et al. 1980). PCBs redistributed from sediment to water will be partitioned in a similar way to fishes and organisms in the open water.

To study the availability to eel of PCBs released from the sediment to water by benthic macroinvertebrates, aquatic model systems were constructed. The systems were composed of sediment contaminated with PCBs, water, macroinvertebrates and eels. To study the uptake of PCBs in fish directly from water, sediments of some systems were screened off with a net. In other systems the fishes were allowed to feed and burrow in the sediment. The role of particles as PCB carriers were studied.

## 2. Materials and methods

Sediment and water were collected in Lake Havgårdssjön situated in South Sweden. The location of the lake and water/sediment data are described elsewhere (Södergren and Larsson 1982). The sediment contained 0.009 ug PCBs/g fresh weight (0.085 ug/g dry weight). Eels (Anguilla anguilla) with an age of approximately four years, fresh weight 1-2 g, were taken in a small brook near Lake Havgårdssjön. The concentration of PCBs in the eels were 0.267 ug/g fresh weight (n=8, SD 0.065) or 12.3 ug/g extractable fat (SD 2.0). Chironomids (Chironomus plumosus-type) were **s**ampled in a small pond in the lake area and contained 0.169 ug PCBs/g fresh weight (12.8 ug/g extractable fat). Tubificids (Tubifex tubifex) were cultivated in the laboratory and contained 0.077 ug PCBs/g fresh weight (20.8 ug/g extractable fat). Eels and macroinvertebrates were acclimatized for 4 weeks at the experimental temperature before start of the experiment.

### 2.1 Experimental set-up

The model systems consisted of 60 l aquarias to which 9 kg of fresh, sieved sediment (mesh size 2 x 2 mm) were added. Water (32 l) was then carefully poured onto the sediment, and the



systems were allowed to equilibrate for one week (Fig 1). The experiment was performed at 8°C. Light was regulated with a photocell, resulting in natural light conditions. PCBs (Clophen A 50 , 24.8 mg dissolved in 1.2 ml of ethanol), were injected through silicon septas in the bottom of the aquarias. The substance was injected at 40 places, 10 mm below the sediment surface, and the systems were left for 2 days to stabilize. About 400 chironomids (2 400 animals/m<sup>2</sup>) and ca 4 300 tubificids (25 000 animals/m<sup>2</sup>) were then added to the systems. The invertebrates were added in numbers to simulate conditions in a eutrophic lake. Some systems were screened off with a net (mesh size 1 x 1 mm) 10 cm above the sediment surface, to prevent eels from direct contact with the sediment. 15 eels were added to each aquaria, and the systems were closed with a glass cover. The systems were kept under reduced pressure (200 mm water column) in order to prevent escape of PCBs. Each system was aerated with a metal capillary located 10 cm above the sediment surface.

## 2.2 Sampling and analytical methods

The experiment was terminated after 77 days and the water was drawn off with a glass siphon without disturbing the sediment surface. Eels were captured with a net, kept in tap water for one hour before being killed. Sediments were carefully mixed, and two subsamples of 20 g were taken for PCB analysis from each aquaria (the macroinvertebrates removed). The remaining sediment was sieved and the macroinvertebrates collected.

Water samples were taken weekly by filtering water through Amberlite XAD-2 (McNeil et al. 1977, Coburn et al. 1977, LeBel and Williams 1980). The filter consisted of 18 x 0.6 cm I.D. glass tubes with 1.4 g air-dried XAD-2 (with plugs of silanized glass wool at both ends). The XAD-2 resin was purified according to McNeil et al. (1977). The filters were prepared according to Coburn et al. (1977). Prior to use the filter was cleaned by eluting with 5 ml acetone, 20 ml of acetone/hexane (1:1) and finally with 10 ml of hexane. The filter was then air-dried. To check the purity of the filter, the final 10 ml portion of hexane

was concentrated to 300  $\mu$ l. The background amounts of the filter was 0.007  $\mu$ g PCBs (n=11, SD 0.002).

The filters were connected to a permanent glass-siphon, inserted in the cover glass of the aquaria (15 cm above the sediment surface, Fig 1), with a teflon tubing connected to a peristaltic pump (Ismatec mp 25GJ-4). About 1 l of water was filtered at each sampling. The filtered water was returned to the aquaria to keep the water volume constant.

The XAD-2 filters were eluted with 2 ml of acetone followed by 20 ml of acetone/hexane (1:1). This procedure removed 96.2% of the PCBs that was adsorbed onto the filter (n=8, SD 3.0).

The effectiveness of the filter was tested by connecting two filters in series. Of the total amount trapped, the first filter collected 86.3% of the PCBs (n=8, SD 2.9). Consequently, one filter was sufficient to sample the PCBs. No differences in the gas chromatographic pattern of PCBs were noticed between the two filters.

The effectiveness of the filters were compared to liquid/liquid extraction. One liter of the aquaria water was extracted with 2 x 30 ml of hexane. The results from the extraction method showed 66.6% (n=8, SD 18.9) of the PCB amounts obtained from the XAD-2 technique.

Samples of the water were cleaned up and analysed according to Södergren (1973). Sediment and macroinvertebrates were extracted, cleaned up and analysed by gas chromatography slightly modified after Södergren (1973). Eels were decapitated, gut and intestines removed, extracted, cleaned up and analysed by gas chromatography slightly modified after Södergren (1973). The minimum detectable quantity of PCBs was 45 pg for individual PCB compounds, and 0.2 ng for Clophen A 50.

At regular intervals water samples were taken for determination of turbidity and particle counting. Turbidity was measured with

a Hach laboratory turbidimeter model 1860. The particles were counted with a Celloscope 302.

### 3. Results

#### 3.1 PCBs in the sediment

The concentration of PCBs in the sediment of the systems ranged from 0.4-1.0 ug/g fresh weight (Tab 1), while the control system showed 0.013 ug PCBs/g.

#### 3.2 Transport to water

A transport of PCBs occurred from sediment to water in all systems except the control (Fig 2). Before the macroinvertebrates were added, the mean concentration of PCBs in the water of the contaminated systems was 0.012 ug/l (SD 0.010). After the macroinvertebrates were added there were an initial increase in PCB concentrations during the first three weeks. Thereafter, the dependence of PCB concentration in the water on time was found not to be significant ( $p > 0.1$ , t-test). This allowed the use of the average concentration over the 11 week period for between treatment comparison. In systems without net the mean concentrations of PCBs in the water were 0.537 ug/l (SD 0.170) and 0.680 ug/l (SD 0.315), respectively. In systems with net, the concentrations were significantly lower ( $p < 0.002$ , Mann-Whitney U-test, two-tailed), 0.106 ug/l (SD 0.043) and 0.242 ug/l (SD 0.112). The PCB concentration in the water of the control system never exceeded 0.007 ug/l.

The concentration of PCBs in the water of the systems was correlated to the turbidity measured as JTU ( $r_s = 0.76$ ,  $p < 0.001$ , Spearman rank correlation) (Fig 3,4). Particles with diameters ranging from 2-40 um were counted at two occasions in the systems. The number of particles was about  $60 \cdot 10^3$ /ml and 70-90% of the particles was in the 2-6 um range. No differences in the particle numbers were observed between the systems.

### 3.3 Uptake in eels

The concentrations of PCBs in eels of systems to which PCBs had been added differed significantly from eels in the control ( $p < 0.002$ , Mann-Whitney U-test, two-tailed) both on fresh weight and extractable fat calculations (Tab 2). No significant differences were recorded in either fresh weight or fat content between eels of different systems ( $p > 0.1$ , t-test).

The macroinvertebrates in the sediment contained 1.5-4.1 ug PCBs/g fresh weight (Tab 3). Based on extractable fat calculations, the animals contained 109-504 ug/g. In systems without net, in which eels were allowed to feed in the sediment, the remaining macroinvertebrates were few. Therefore, PCBs were determined in a composite sample of chironomids and tubificids.

No differences were observed in the gas chromatographic pattern of PCBs added and that recovered in sediment, water, macroinvertebrates or fish.

### 4. Discussion

In the systems a transfer of PCBs occurred from sediment to water which depends on at least two mechanisms, desorption and bioturbation (animal activity in the sediment, Södergren and Larsson 1982). A desorption of PCBs from sediment to water, *e.g.* a sediment/water partitioning, depends among other things on the composition of the sediment (Steen *et al.* 1977, Halter and Johnson 1977, Wildish *et al.* 1980). A sediment of high organic content adsorbs lipophilic compounds stronger than a sediment of a minerogenic character. The desorption of PCBs from sediment to water is probably reinforced by benthic macroinvertebrate activity, thus increasing the outflow of PCBs from the sediment, *e.g.* shift the sediment/water partitioning. This shift could be a result of changed physical/chemical conditions in the sediment or by an increase in the area of the sediment/water interface by the burrowing activity of the invertebrates.

The levels of PCBs in the water were higher in systems without net compared to the screened systems. When eels are feeding in the sediment, the animals resuspended sediment particles to which PCBs were adsorbed. This was especially true during the first three weeks; after that the eels burrowed in the sediment and showed minor activity. Therefore, the influence on PCB levels in the water by the activity of the eels was low during the major part of the experiment. In general the eels showed low activity (swimming, feeding) due to the low temperature.

The PCB concentrations in the water fluctuated during the 11-week period, but showed no sign to increase nor decrease. This was probably due to the relatively stable conditions in the sediment. A change in temperature or number of animals etc. would probably change the dynamics of the transport process.

The amounts of particles in the water determined the levels of PCBs. The particles originated from the sediment, that contained the major fraction of the PCB compounds. Benthic macroinvertebrates and/or eels induced a transport of PCB containing particles across the sediment/water interface. This was supported by the fact that no differences were observed in the relation of peaks in the gas chromatograms of sediment and water. When desorption is the dominating process less lipophilic PCB compounds (e.g. less chlorinated ones) are more readily released from sediment to water, than the more lipophilic ones of the Clophen A 50 mixture (Halter and Johnson 1977).

Eels in the screened systems accumulated PCBs 10-30 times the concentrations found in eels of the control. Since the eels in the screened systems were separated both from sediment and from PCB uptake via the food chain, the uptake occurred from the water. The uptake include at least two processes: 1. Adsorption or absorption via the water, e.g. water/fat partitioning in the fishes mainly through gills or skin (Hamenlink et al. 1971, Sagiura et al. 1978). 2. Uptake from particles through ingestion or uptake directly from particles by adsorption/exchange (Omann and Lakowicz 1981).

Eels that were allowed to feed in the sediment showed



concentrations of 27-50 times those found in the control eels. A considerable amount of the benthic macroinvertebrates was consumed by the eels in the non-screened systems. The uptake of PCBs from sediment to invertebrates is a rather fast process (days) (Courtney and Langston 1978, McLeese et al. 1980). Therefore, the PCB pool of the macroinvertebrates was available for the eels during the experiment. The eels were observed to feed to at least day 60. Uptake of PCBs in the eels is a result of an accumulation from food, uptake directly from sediment and/or uptake via the water.

The mean PCB concentration in eels separated from the sediment was 277.5 ug/g (extractable fat). In eels that were allowed to feed and burrow in contaminated sediment, the concentrations were about two times higher (471.6 ug/g). Thus, despite their feeding and burrowing activity in the sediment, these eels showed lower concentrations than expected, compared to eels of the screened systems. I therefore suggest that the major route for PCB uptake in the eels was via the water, either by water/fat partitioning in the eels and/or by particles. However, at a higher temperature the pattern may be different, as the activity and the metabolism of the fishes are raised. In that case uptake via the food could be of greater importance than uptake from water.

The study indicate that lipophilic, persistent pollutants, as PCBs, are available for aquatic organisms even if no food chain transport occur. The main pathways for PCB uptake in organisms seems to be water/fat partitioning; through water directly or from contaminated particles in the water. The mechanism of food web transport could raise PCB concentrations over the expected partitioning levels, but only to a limited extent. Consequently, contaminated sediment in lakes and water courses may act as a source of PCBs to fish.

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| SYSTEM | TREATMENT   | PCBs,<br>ug/g fresh weight | PCBs,<br>ug/g dry weight |
|--------|-------------|----------------------------|--------------------------|
| 1      | control     | 0.013                      | 0.085                    |
| 2      | without net | 1.007                      | 6.237                    |
| 3      | without net | 0.956                      | 6.032                    |
| 4      | with net    | 0.701                      | 4.640                    |
| 5      | with net    | 0.434                      | 3.138                    |

Tab 1. PCBs in the sediment of the model systems. Two replicates were analysed from each system.



| SYSTEM | TREATMENT   | PCBs,<br>ug/g fresh weight | PCBs,<br>ug/g extractable fat |
|--------|-------------|----------------------------|-------------------------------|
| 1      | control     | 0.267 (sd 0.065)           | 12.3 (sd 2.0)                 |
| 2      | without net | 7.245 (sd 1.024)           | 330.0 (sd 140.0)              |
| 3      | without net | 14.145 (sd 1.728)          | 613.2 (sd 131.1)              |
| 4      | with net    | 2.543 (sd 0.509)           | 147.0 (sd 43.0)               |
| 5      | with net    | 8.926 (sd 2.033)           | 408.1 (sd 182.3)              |

Tab 2. PCBs in eels of the model systems. 8 eels were analysed from each system.

| SYSTEM | ANIMALS                     | TREATMENT   | PCBs,<br>ug/g fresh weight | PCBs,<br>ug/g extractable fat |
|--------|-----------------------------|-------------|----------------------------|-------------------------------|
| 1      | tubificids<br>chironomids   | control     | 0.077<br>0.169             | 20.8<br>12.8                  |
| 2      | tubificids +<br>chironomids | without net | 3.798                      | 504.1                         |
| 3      | tubificids +<br>chironomids | without net | 4.119                      | 418.7                         |
| 4      | tubificids<br>chironomids   | with net    | 1.468<br>2.315             | 109.5<br>372.7                |
| 5      | tubificids<br>chironomids   | with net    | 1.522<br>2.435             | 128.8<br>404.0                |

Tab 3. PCBs in macroinvertebrates of the model systems.

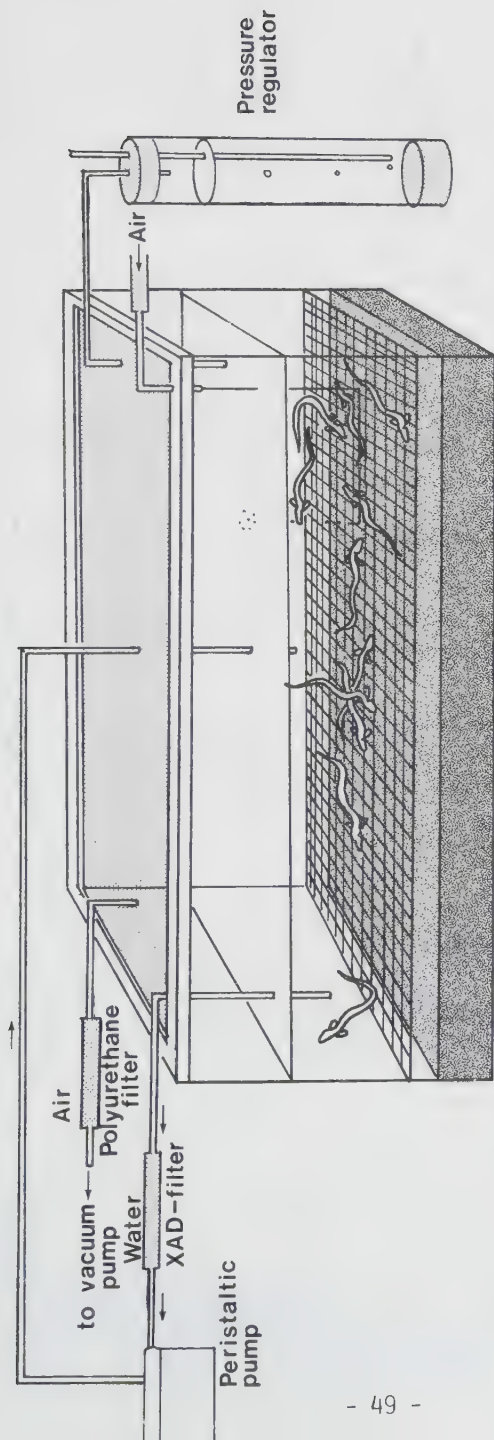


Fig 1. Closed aquarium system to study the recirculation of PCBs from sediment to water and to follow the uptake in eels. Some systems were screened off by a net in order to prevent eels from direct contact with the sediment. Water samples were taken by passing the water through Amberlite XAD-2 filter. The system was kept under reduced pressure with a vacuum pump in order to prevent escape of PCBs. The air from the system was continuously passed through a filter consisting of polyurethane foam. Reduced pressure was kept at 200 mm water column with a pressure regulator.

Fig 2. PCBs in the water of the model systems during the 11-week experiment.



Fig 3. PCBs and turbidity in the water versus time  
in the four model systems.

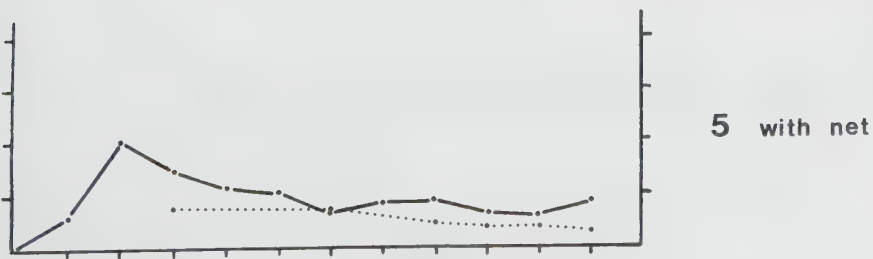
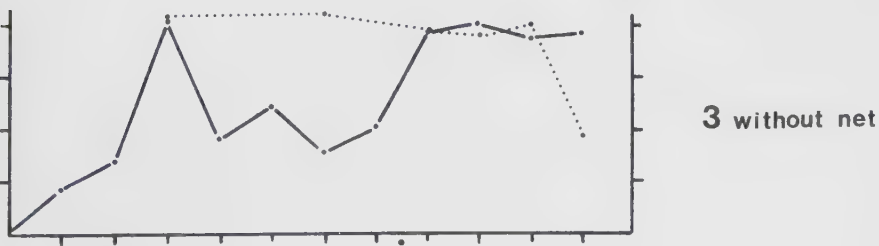
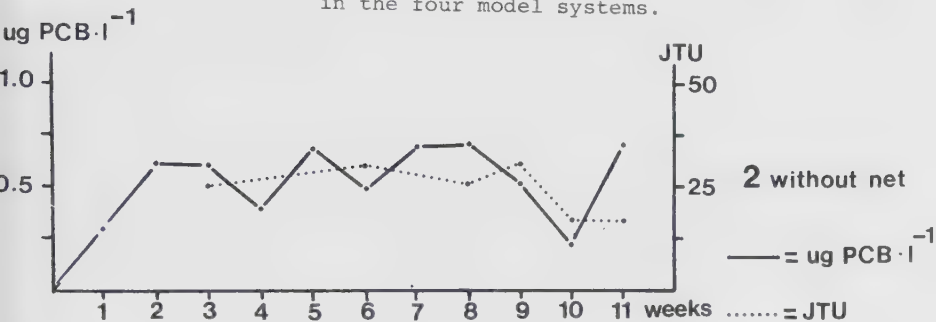
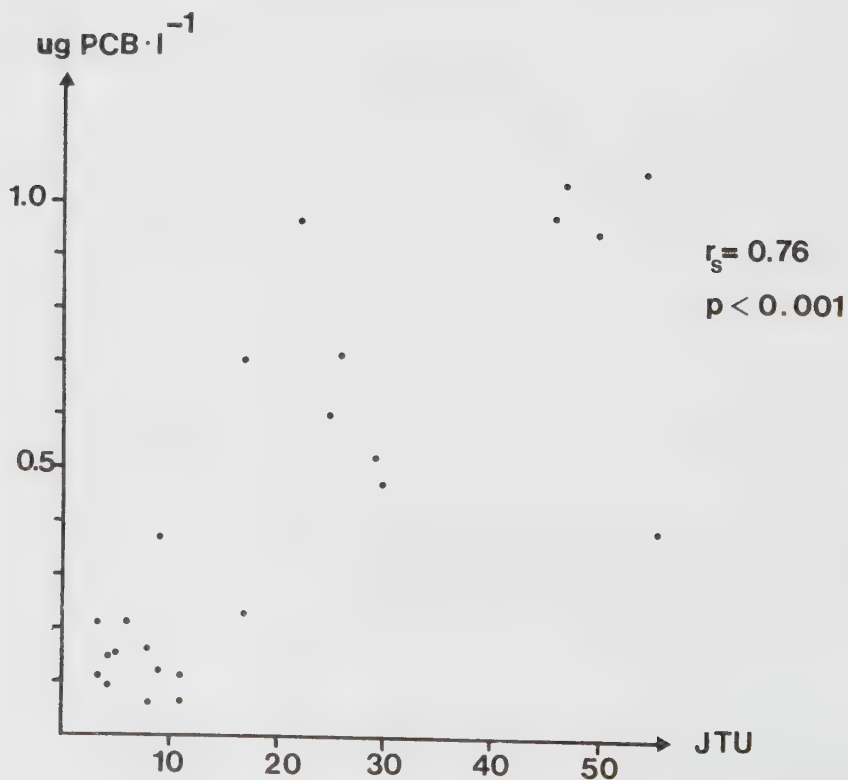


Fig 4. Correlation of PCB concentration and turbidity  
in the water of the model systems.





PCBs (CLOPHEN A 50) CHANGE COMPOSITION WHEN TRANSPORTED  
FROM SEDIMENT TO AIR IN AQUATIC MODEL SYSTEMS.

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## Abstract

PCBs (Clophen A 50) were added to the sediment of laboratory model systems composed of sediment, water, benthic macroinvertebrates and fish. Part of the PCBs left the sediment and a concentration of 0.2-0.7 ug/l was obtained in the water.

The transport of PCBs from water to air includes at least two processes: volatilization and jet drop transport. Volatilization (as indicated by PCBs trapped on polyurethane foam filters) resulted in a transport of 0.2-1.0 ug PCBs·week<sup>-1</sup> to air. Less chlorinated PCBs, i.e. tetrachlorobiphenyls, were transported to the air at a higher extent than more chlorine-substituted PCBs.

Transport of PCBs by jet drops from bursting bubbles (as indicated by the amount of PCBs found on jet drop impactors) was of the same magnitude as volatilization, but the proportion of PCB compounds trapped by the impactor plates was identical to that of sediment and water. The process seems mainly to transfer PCB containing bulk water and particles to the air.

The results suggest that contaminated sediment of lakes and water courses may act as a source of PCBs to the atmosphere.

## 1. Introduction

PCBs (polychlorinated biphenyls) are found within the global ecosystem in both biotic and abiotic reservoirs. Atmospheric transport of the compounds seems to be of great importance. PCBs have been detected in air in several areas (1, 2, 3, 4), in rain (5), in dry deposition (6) and in foliage (taken up from air (7)). Most of the air-borne PCB fraction is in the vapor phase while a smaller fraction is associated to particles (1, 3, 8).

The most evident sources of atmospheric PCBs is the combustion of PCB-containing materials and the release of PCBs from industries (9). However, the question has recently been raised whether large water bodies, like Lake Michigan, can act as a source for PCB transport to air rather than as a sink (8).

The transport of PCBs from water to air includes volatilization (10, 11, 12, 13), codistillation (14) and jet drops from bursting bubbles (15, 16, 17). Jet drop transport could include at least two processes whereby lipophilic compounds are removed from the water phase: 1. Solved or emulsified compounds adsorb to rising microbubbles in the water. 2. Particles, to which the compounds are associated, adsorb to the rising microbubbles. The bubbles collapse at the water/air interface and eject jet drops containing the solved compounds or particles. Jet drops may also eject compounds enriched in the surface microlayer (18). The effectiveness of removing PCBs from the water to the air by bubbles was demonstrated by Colenutt and Thorburn (19). A transport of PCBs from sediment to air has been shown to occur in aquatic model systems (18, 20).

PCBs present in the water of lakes and water courses originate from several sources including precipitation, land run-off, industrial and municipal waste discharges and accidental spills. The sediments of lakes and oceans are generally considered as ultimate sinks for PCBs and the persistent residues accumulated in the sediments are thought to be inactive. However, several processes may redistribute PCBs from the sediment to the water. These processes include: desorption (21, 22), resuspension of particles from the sediment (23, 24, 25), altered physical and chemical

conditions in the sediment such as pH, salinity, organic content etc. (26) and the activity of benthic macroinvertebrates in the sediment (18).

The aim of this experiment was to study the transport of PCBs from sediment to water and to air in aquatic laboratory model systems. To enhance the transport of PCBs from sediment to water benthic macroinvertebrates and fish were added. Composition of the PCBs (Clophen A 50) in sediment, water, surface microlayer and air was investigated, to determine if the PCB mixture were changed in the transport processes (i.e. if transport rates were higher for certain chlorobiphenyls).

## 2. Materials and methods

Sediment and water was collected in Lake Havgårdsjön, southern Sweden. The location of the lake and the water and sediment data is described elsewhere (18). The sediment contained 0.009 ug PCBs/g fresh weight (0.085 ug/g dry weight). Eels (Anguilla anguilla) approximately four years old and weighing 1-2 g, were taken from a small brook near Lake Havgårdssjön. Chironomids (Chironomus plumosus-type) were taken from a small pond near the lake and tubificids (Tubifex tubifex) were cultivated in the laboratory.

### 2.1 Experimental set-up

The model systems consisted of 60-l aquaria, to which 9 kg of fresh, sieved sediment (mesh-size 2 x 2 mm) was added. Water (32 l) was carefully poured onto the sediment and the systems were allowed to equilibrate for one week (Fig 1). The experiment was performed at 8°C. Light was regulated with a photocell to simulate natural light conditions. PCBs (Clophen A 50), 24.8 mg solved in 1.2 ml ethanol, were injected into the sediment through silicon septa located in the bottom of the aquaria. The substance was injected at 40 places, 10 mm below the sediment surface, and the systems were left for two days to stabilize. About 400 chironomids (2 400 animals/m<sup>2</sup>) and about 4 300 tubificids (25 000 animals/m<sup>2</sup>) were then added to the systems. Organisms were added in numbers which

simulate conditions in eutrophic lakes. Some systems were screened off with a net (mesh size 1 x 1 mm) 10 cm above the sediment surface to prevent eels from direct contact with the sediment. Fifteen eels were added to each aquarium and the systems were closed with a glass cover. The systems were kept under reduced pressure (200 mm water column) in order to prevent escape of PCBs. Each system was aerated with a metal capillary located 10 cm above the sediment surface (3-5 bubbles/second, about 1-3 mm in diameter). The microbubbles produced by the capillary resulted in jet drops.

## 2.2 Sampling and analytical methods

PCBs in the water of the systems were sampled weekly by passing the water through Amberlite XAD-2 filters (27, 28, 29). Preparation of the filters, the extraction procedure and filter efficiency are described elsewhere (30). The filters were connected to a glass siphon, inserted through the cover glass of the aquaria (15 cm above the sediment surface (Fig 1)), with a teflon tubing connected to a peristaltic pump. About 1 l of water was filtered through the resin at each sampling. The filtered water was returned to the aquaria to keep the water volume constant.

Surface microlayers of the systems were sampled weekly using a teflon plate (31). The transport of PCBs from water to air by jet drops was followed by collecting the drops on a hydrophilic teflon impactor ( $A=50.2 \text{ cm}^2$ ), 7 cm above the surface of the water (18). The impactors were sampled weekly. The teflon plates for surface microlayers and jet drop impactors were extracted with 2 x 5 ml acetone/hexane (1:1) in an ultrasonic bath for 10 minutes.

Air leaving the systems was passed through a filter consisting of polyurethane foam (2, 32, 33). The filters were changed weekly. Porous polyurethane foam (PPF, density  $0.028 \text{ g/cm}^3$ ) was cut into plugs (10 mm x 100 mm) (33) and inserted into glass tubes. The plugs were cleaned with acetone/hexane (1:1) followed by hexane. The hexane was evaporated to 300  $\mu\text{l}$ , cleaned-up and the PCB content determined by gas chromatography. Blank value for the plugs was  $0.013 \text{ ug PCBs}$  ( $n=11$ ,  $SD 0.015$ ). Air samples were taken by connecting the PPF-filters to glass tubes inserted in the cover glasses of

the aquaria. The filters were connected to teflon tubing leading to a vacuum pump. In one week, about 3 m<sup>3</sup> air passed the filters.

The PCB residues on the filters were extracted in 2 x 10 ml acetone/hexane (1:1) in an ultrasonic bath for 10 minutes. This procedure removed 86.2% of the Clophen A 50 (n=8, SD 3.1).

The efficiency of the filters was tested by connecting two filters in series from the aquaria. The first filter collected 90.5% of the PCBs (n=8, SD 10.9). One filter was subsequently considered satisfactory for the following sampling procedures.

To check whether filter extraction was selective for the PCB compounds first eluted in the gas chromatographic analyse, Clophen A 50 (0.594 ug solved in 0.1 ml of hexane) was injected into the filters. The hexane was then evaporated, the filters were connected to the aquaria in the described way, exposed for one week and extracted similarly to the PPF-filters mentioned earlier. No selection of PCB compounds was recorded.

The experiment was terminated after 77 days and the water was drawn off with a glass siphon without disturbing the sediment surface. Eels were captured with a net and kept in tap water for one hour before being killed. Sediments were carefully mixed and two subsamples of 20 g were taken from each aquaria for PCB analysis (the macroinvertebrates removed). The remaining sediment was sieved and the macroinvertebrates collected.

PCBs in sediments were extracted according to Södergren (34). PCB extracts of sediment, water, jet drop impactors, surface microlayers and PPF-filters were evaporated to 300-1000 ul and cleaned-up according to Södergren (34).

The contents of PCBs in the extracts were determined by gas chromatography, using standard procedures (35, 36). The minimum detectable quantity of PCBs was 45 pg for individual PCB compounds and 0.2 ng for Clophen A 50.



### 3. Results

PCBs injected into the sediment were transferred to the water and air. In the water, the PCB concentrations ranged from 0.2 ug/l to 0.7 ug/l during the eleven-week experiment (Fig 2). Before the macroinvertebrates were added, the mean concentration of PCBs in the water of the systems was 0.012 ug/l (SD 0.010). In the control (no PCBs added to the sediment), the PCB concentrations in the water never exceeded 0.007 ug/l. The PCB concentrations in the sediment of the systems ranged from 0.4-1.0 ug/g fresh weight (Tab 1).

PCBs were trapped by the PPF-filters of the systems (Fig 3). The transport rates were highest in the beginning of the experiment; later the rates varied between 0.2-1.0 ug·week<sup>-1</sup>. The control released 0.013 ug PCBs·week<sup>-1</sup> to the air (SD 0.015).

Clophen A 50 and Aroclor 1254 will under standardized gas chromatographic conditions produce 12-14 distinct peaks (Fig 4). When the PCB compounds were transported from sediment to air, the gas chromatographic pattern of Clophen A 50 was changed. In comparison to the PCB mixture originally added, the first two eluted peaks (0.47 and 0.70 relative to DDE (35)) contained 55.7% of the total mixture (Fig 5). These two peaks of Clophen A 50 represent tetrachlorobiphenyls (35, 37). The later eluted peaks (3-10) represent mostly penta- and hexachlorobiphenyls. No differences were observed in the gas chromatographic patterns of sediment or water when compared to the PCBs originally injected. This was also the case for the gas chromatographic patterns of PCBs deposited on jet drop impactors. When compared to the gas chromatographic patterns of PCBs trapped on PPF-filters, no shift towards earlier eluted PCB compounds was recorded (Fig 6).

In the surface microlayers about 0.05 ug PCBs·dm<sup>-2</sup> were found (Fig 7a). In the control system the mean amount was 0.015 ug PCBs·dm<sup>-2</sup> (SD 0.009).

The transport rate of PCBs to jet drop impactors ranged from 0.20 to 1.70 ug·dm<sup>-2</sup>·week<sup>-1</sup> (Fig 7b). In the reference system the mean rate was 0.014 ug PCBs·dm<sup>-2</sup>·week<sup>-1</sup> (SD 0.008).

The amounts of PCBs taken up by the macroinvertebrates and fish are reported elsewhere (30).

#### 4. Discussion

The basis for separation by gas chromatography and quantitation of PCBs by electron capture detectors has been extensively studied (35, 37, 38). Several attempts to intercalibrate gas chromatographic methods have been made and more or less standardized methods are used to describe the chromatographic behaviour of for example Clophen A 50 or Aroclor 1254 (35, 36). While capillary columns have proved dramatically to increase the resolution, the methods to quantitate all peaks detected still are to be refined, as well as the reproducibility when large numbers of analysis are run. In this respect packed columns are still valid.

The first two peaks (eluted after 0.47 and 0.70 relative to DDE) normally contain 7.1-7.4% and 14.7-11.0% of the total Aroclor 1254 or Clophen A 50, respectively (35, 39). They represent together about 21.8% of Aroclor 1254 and 18.4% of Clophen A 50.

In the air of the systems (as represented by the amounts found trapped by the PPF-filters), the first two peaks contained 55.7% of Clophen A 50. The shift in the PCB pattern of air-borne residues, towards earlier eluted PCB compounds (i.e. tetrachlorobiphenyls), indicates that less chlorinated PCBs are transported to air to a greater extent than compounds substituted with several chlorine atoms. This has been shown for individual PCB compounds (not present in a mixture like Clophen A 50) where tetrachlorobiphenyls were transported to air to a greater extent compared to hexa- and octachlorobiphenyls (20).

The composition of the PCB mixture underwent no changes when transported to the air via jet drops from bursting bubbles. I therefore assume that volatilization direct the transport of PCBs from water to air (i.e. from water to PPF-filters). The transport of PCBs by jet drops from water to air was probably dominated by a transport of subsurface water and particles to the impactor plates, since the pattern of PCBs trapped by the plates was almost identical to that of the water.

The higher proportion of less chlorinated PCBs (i.e. tetrachlorobiphenyls) retained on the PPF-filters may be a result of a higher vaporization rate (40) and volatilization rate (8), compared to more chlorine-substituted PCBs.

The continuous mixing of the water by microbubbles is important for the volatilization transport of PCBs from the water phase to the air. This leads to a transfer of lipophilic compounds from the water to the water/air interface (41) making them 'available' for transport to the air. Due to the hydrophobic character of the surface microlayer (41), hydrophobic compounds like PCBs are enriched, with the surface microlayer functioning as a barrier between the water and air. The continuous disturbance of the microlayer by bubbles enhances transport of the compounds to the air. The bubble production also increases the surface area of the water exposed to the air, which probably increases the volatilization rate of PCBs.

Transport of PCBs from the water to the air seems to be rather constant over time and is related to the concentration of PCBs in the water, though no significant correlation could be found. A higher concentration of PCBs in the water resulted in higher amounts trapped on the PPF-filters, at least in the second half of the experiment. Consequently, a seasonal variation of PCBs in lake water would result in a corresponding variation in the overlying air.

The limiting process in the transport of PCBs from sediment to air is probably the transfer of PCBs from sediment to water. The transport of the compounds across the sediment/water interface is enhanced by benthic macroinvertebrate activity in the sediment (18, 19). This activity results in a transport of PCB containing particles to the water (30). A PCB contaminated sediment with low macroinvertebrate activity, where desorption dominates the transport processes, results in lower transport rates of PCBs to the water (18) and consequently to air.

PCBs present in sea water correspond to Aroclor 1260, containing PCB compounds substituted with five chlorine atoms or more (1). Is this a result of the higher transport rate to air of less chlorinated PCBs, i.e. mono- tetrachlorobiphenyls, as this experiment indicates? This would lead to a decreased exposure to aquatic organisms of these compounds, and consequently a higher uptake/partitioning of more chlorine-substituted PCBs in the animals. Accordingly, it would give an alternative or additive explanation for the presence of more chlorine-substituted PCBs in aquatic organisms, that has hitherto been explained by metabolism of the less chlorine-substituted PCBs.

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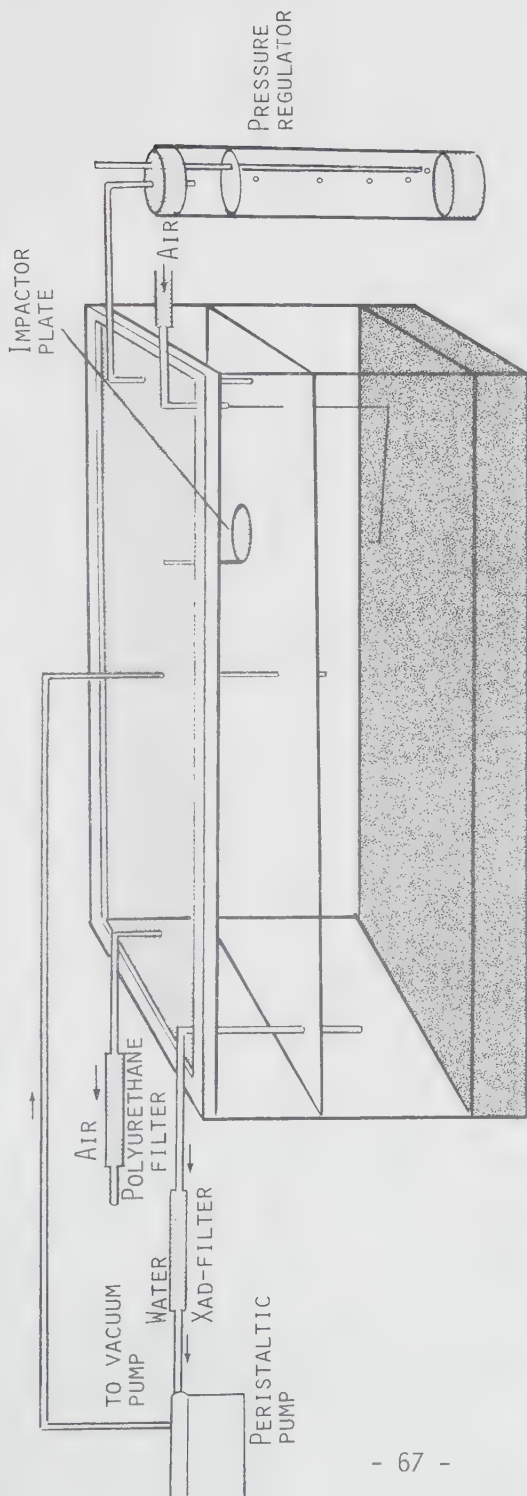


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| SYSTEM | TREATMENT   | PCBs,<br>ug/g fresh weight | PCBs,<br>ug/g dry weight |
|--------|-------------|----------------------------|--------------------------|
| 1      | control     | 0.013                      | 0.085                    |
| 2      | without net | 1.007                      | 6.237                    |
| 3      | without net | 0.956                      | 6.032                    |
| 4      | with net    | 0.701                      | 4.640                    |
| 5      | with net    | 0.434                      | 3.138                    |

Tab 1. Concentrations of PCBs in the sediment of the model systems.  
Two replicates were analysed from each system.

Fig 1. Closed aquarium system to study the recirculation of PCBs from sediment to water and air. PCBs in the water were sampled by passing the water through Amberlite XAD-2 filter. The system was kept under reduced pressure with a vacuum pump in order to prevent escape of PCBs. Air leaving the systems was continuously passed through a filter consisting of polyurethane foam. Reduced pressure was kept constant at 200 mm water column with a pressure regulator. PCBs in jet drops from bursting bubbles were trapped on an impactor plate placed 7 cm above the water surface.



PCBs:  
 $\mu\text{g} \cdot \text{l}^{-1}$

Fig 2. Concentrations of PCBs in the water during the 11-week experiment. System 2 and 3 were without net, 4 and 5 were screened.



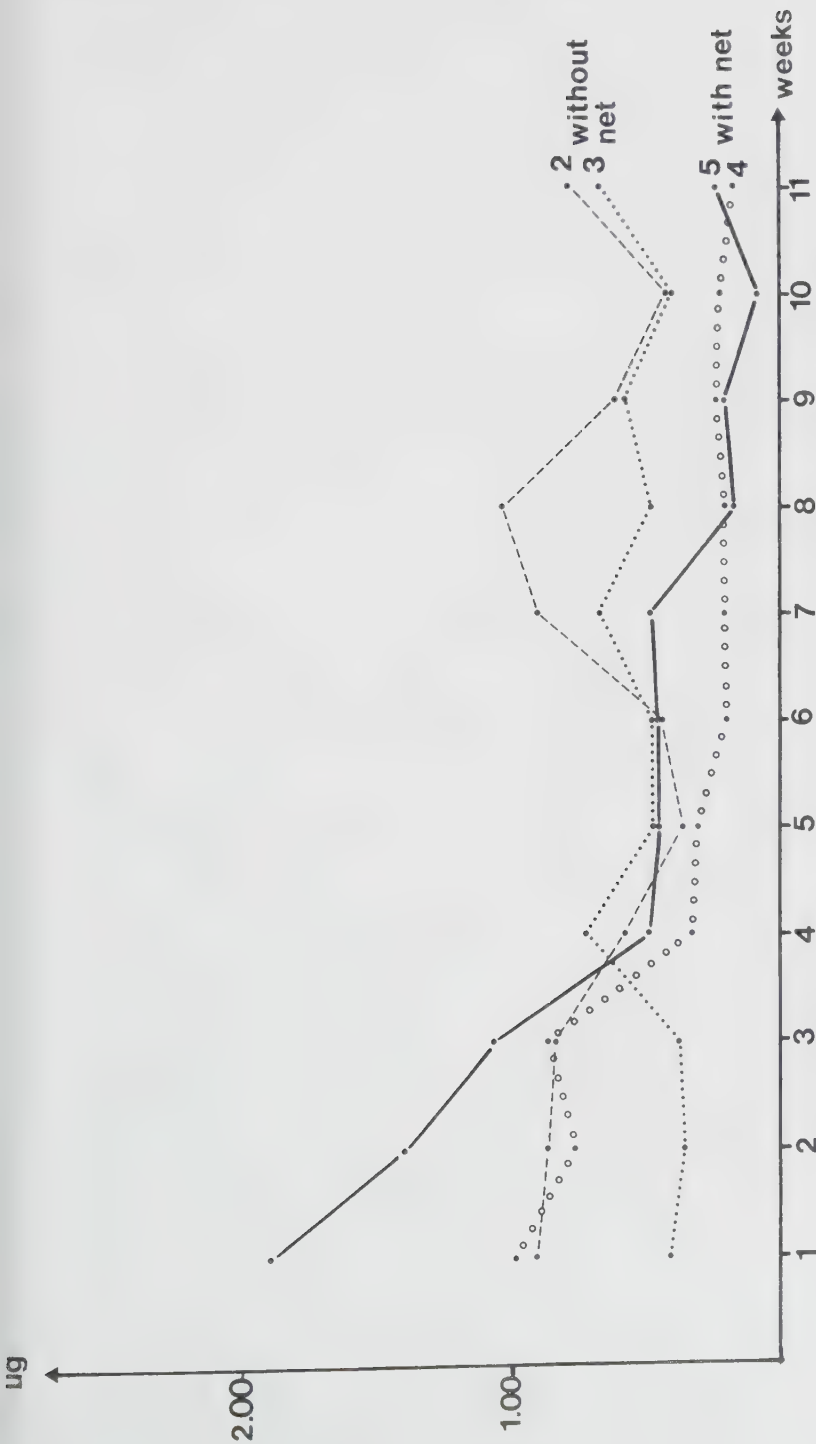
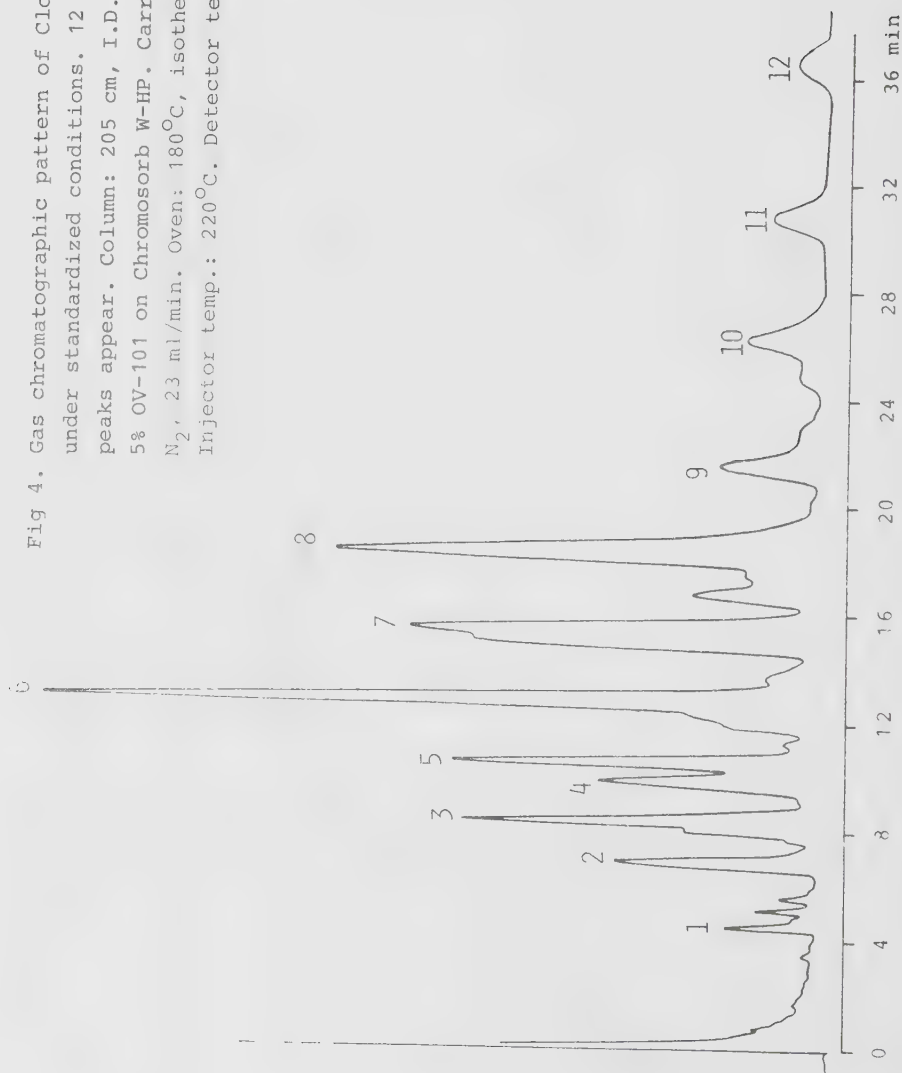


Fig 3. PCBs in the air (found on PPF-filters) of the systems.

Fig 4. Gas chromatographic pattern of Clophen A 50 under standardized conditions. 12 distinct peaks appear. Column: 205 cm, I.D. 1.2 mm, 5% OV-101 on Chromosorb W-HP. Carrier gas: N<sub>2</sub>, 23 ml/min. Oven: 180°C, isothermal. Injector temp.: 220°C. Detector temp.: 240°C.





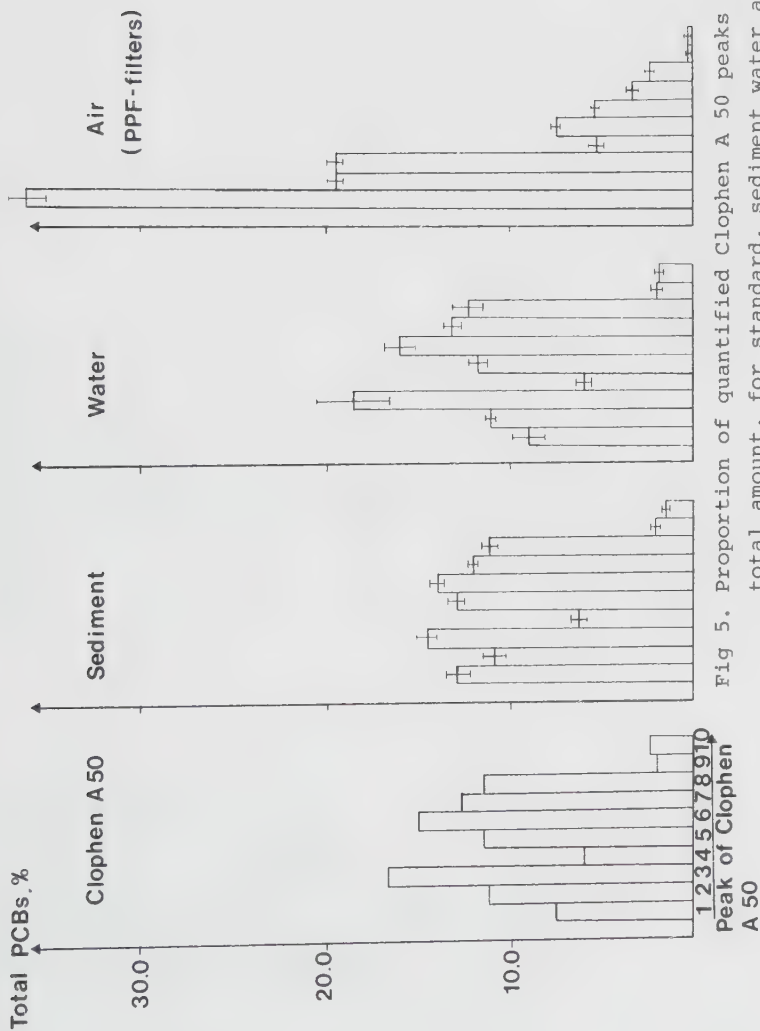


Fig 5. Proportion of quantified Clophen A 50 peaks as percent of total amount, for standard, sediment, water and air (as indicated by the amounts found on PPF-filters). 10 PCB peaks are presented in the figure since peak 11 and 12 not were detectable in air. 8 samples were analysed from each compartment. Vertical bars denote standard deviation.

Total PCBs. %

30.0

20.0

10.0

Air  
(Jet drop impactors)

Air  
(PPF-filters)

1 2 3 4 5 6 7 8 9 10  
Peak of Clophen A 50

Fig 6. Proportion of quantified Clophen A 50 peaks as percent of total amount, for PCBs found on jet drop impactors and PPF-filters. 8 samples were analysed from each compartment. Vertical bars denote standard deviation.

Fig 7a. PCBs found in the surface microlayers of the systems during the 11-week experiment.

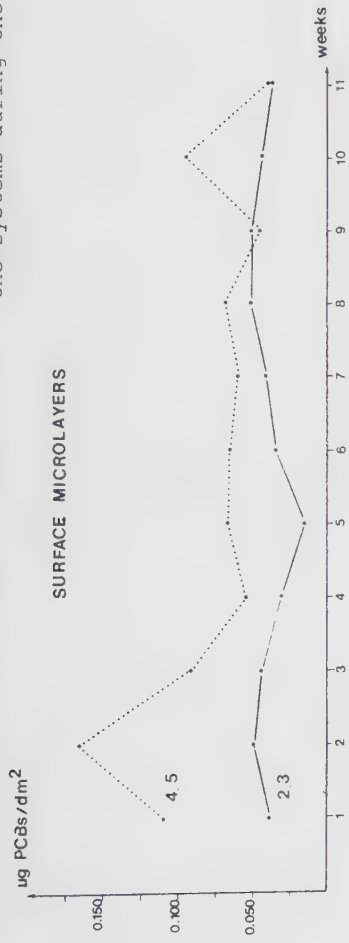
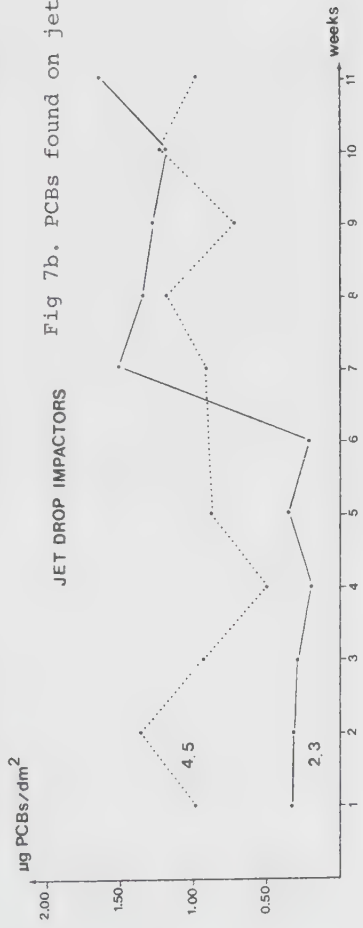


Fig 7b. PCBs found on jet drop impactors.





TRANSPORT OF PCBs FROM AQUATIC TO TERRESTRIAL  
ENVIRONMENTS BY EMERGING CHIRONOMIDS.

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## Abstract

The transport of PCBs from sediment to air by emerging chironomids (Chironomus plumosus-type) was studied in aquatic laboratory model systems. Uptake of PCBs from the sediment by chironomid larvae was directly related to the concentration of PCBs in the sediment. When the larvae metamorphosed to adults the PCB compounds were concentrated and transferred from the aquatic to the terrestrial environment. A minor part of the compounds was retained in the exuviae. In a field study, transport of PCBs by chironomids from the aquatic to the terrestrial environment was estimated at  $20 \text{ ug PCBs/m}^2\text{-year}$ . The results suggest an additional way in which terrestrial predators that feed on emerging aquatic insects whose larval stage is in contaminated sediment, are exposed to organochlorine residues.

## 1. Introduction

It is known that PCBs (polychlorinated biphenyls) are taken up by benthic macroinvertebrates from contaminated sediment (Nimmo et al. 1971, Fowler et al. 1978, McLeese et al. 1980, Courtney and Langston 1978, Södergren and Larsson 1982). The uptake is governed by processes such as ingestion of contaminated sediment particles (Nimmo et al. 1971), absorption of PCBs from interstitial water (McLeese et al. 1980), absorption of PCBs leached to the water (Nimmo et al. 1971) and the uptake/exchange of PCBs directly from sediment particles (Omann and Lakowicz 1981, Larsson, in press).

Aquatic chironomids (Diptera: Chironomidae) are an important food resource for many predators, e.g. fish and diving ducks and seasonally for terrestrial insectivorous birds. With an abundance of 10 000-40 000 individuals/m<sup>2</sup>, particle feeding chironomids like Chironomus plumosus and Chironomus anthracinus may dominate the limnic profundal bottom fauna (Jonasson 1972). Could these aquatic insects act as a link between deposited persistent pollutants in the sediment of aquatic environments and terrestrial predators?

To investigate this, the transport of PCBs from sediment to air by emerging chironomids was studied in laboratory model systems. In order to verify the laboratory study, a field experiment was conducted near a southern Swedish sewage plant.

## 2. Materials and methods

### 2.1 Laboratory studies

Sediment cores were taken in Lake Havgårdssjön, situated in southern Sweden. The cores with an overlying water phase were taken with a Kajak-type corer and were studied without being removed from the sampling tubes (Södergren and Larsson 1982). The sediment cores were regarded as undisturbed. The sediment of Lake Havgårdssjön contained 0.005 ug PCBs/g fresh weight (0.027 ug PCBs/g dry weight <sup>105°C</sup>). The organic content of the sediment (the loss of ignition) was 21.4% (n=18, SD 4.6). Other sediment data and the



water chemistry of the lake are described elsewhere (Södergren and Larsson 1982). Chironomids (Chironomus plumosus-type) were taken in a small pond in the lake area and contained 0.054 ug PCBs/g fresh weight (4.7 ug PCBs/g extractable fat).

The cores were kept at 6°C in the dark. PCBs (Clophen A 50) were injected into the cores through silicon septas in the wall and the substances (solved in 100 ul of ethanol) were spread evenly 10 mm below the sediment surface. Four main concentration levels of PCBs in the sediment were obtained, with four replicates at each level. Two systems were kept as controls (no PCBs added). The systems were gently aerated with a metal capillary.

After a stabilization period of one week, 80-100 chironomid larvae were added to each system.

After 8 weeks, the systems were moved and kept in the light at a temperature of 20°C. The temperature was slowly raised from 6°C to 20°C in a water bath. After two days the chironomids started pupaeting and emerging. Adults and exuviae were sampled daily, put in glass vials and deep frozen.

The experiment was terminated after 10 weeks. The sediment of each system was mixed and subsamples taken for PCB analysis. The remaining sediment was sieved and the chironomid larvae collected. Sediment (20 g) and chironomids (0.5-1.0 g) were extracted, cleaned-up and analysed by gas chromatography (Södergren 1973).

Chironomid larvae, exuviae or adults from two replicates were pooled together in order to get enough material for PCB analysis. Therefore, a mean of the PCB concentration in the sediment of the replicates were calculated (Tab 1).

## 2.2 Field studies

Sediment, chironomid larvae and adult chironomids were taken near a sewage plant in southern Sweden. Sediment samples were collected with a Kajak-type corer and the upper 25 mm of the sediment core

taken for PCB analysis. Chironomid larvae were collected with an Ekman dredge. Adult chironomids were caught with a net, when mass-swarmed at night.

### 3. Results and discussion

The uptake of PCBs from limnic sediments by chironomid larvae was directly related to PCB concentrations in the sediment ( $r^2=0.97$ ,  $F=254$ ,  $p<0.001$ , Fig 1). The concentration factor, the slope of the linear regression, showed a low variation ( $4.23\pm0.629$ ,  $\text{mean}\pm95\%$  CL) within the PCB levels studied (0.005 to 13.76  $\mu\text{g}$  PCBs/g fresh weight of sediment). This indicates that the main process of PCB uptake in the larvae was physical/chemical, *i.e.* a partitioning of the PCB compounds between sediment/interstitial water and the animals (Hamelink *et al.* 1971, Clayton *et al.* 1977, Pavlou and Dexter 1979). A more active uptake, by for instance ingestion of contaminated sediment particles and an active uptake in the gut should result in a larger variation in the concentration factor. However, it is reasonable to assume that the process in fact is described by a curvilinear function, and that the curve rises to a saturation level not reached in this experiment (Moriarty 1975). A direct relationship was also found between the PCB concentration in the sediment and concentrations in adult chironomids and exuviae ( $r^2=0.80$ ,  $F=28$ ,  $0.001<p<0.005$  and  $r^2=0.74$ ,  $F=20$ ,  $0.001<p<0.005$ , Fig 1).

When chironomid larvae metamorphosed to adults the PCB compounds were concentrated (Tab 1, Fig 1) and a concentration factor ( $\frac{\mu\text{g PCBs/g fresh weight of adults}}{\mu\text{g PCBs/g fresh weight of larvae}}$ ) of 4.6 (SD 2.4) was obtained. When the chironomid larvae emerged, their weight was reduced by a factor of 3.8 (from 27.8 to 7.3 mg). The exuviae retained 17% ( $n=8$ , SD 9) of the PCB compounds. Consequently, the loss of weight and the small amount of PCBs retained in the exuviae explains the increase in concentration during the larva to adult process. However, when based on extractable fat calculations, the concentration factor was significantly lower (1.8,  $n=8$ , SD 1.0, Mann-Whitney U-test, one-tailed). This was due to the higher fat content of adult chironomids (2.9%,  $n=10$ , SD 0.4) compared to the fat content of the larvae (1.1%,  $n=10$ , SD 0.2). Accordingly, the PCB compounds were 'diluted' in the fat of adult chironomids.

The concentration of PCBs during the process from larva to adult is important for the transport of the compounds from aquatic to terrestrial environment. Adult chironomids consumed by insectivorous birds may contribute a considerable amount of chlorinated hydrocarbons to their diet.

No changes were observed in the PCB mixture originally added and that found in sediment or chironomids.

In the field, chironomid larvae contained 0.114 ug PCBs/g fresh weight (n=5, SD 0.018, Tab 1) at a sediment concentration of 0.039 ug PCBs/g fresh weight (n=7, SD 0.025). The concentration in the larvae was lower than that predicted by the laboratory study. This may be a result of different properties of the sediment used in the laboratory and in the field studies. Sewage sludge of high organic content more firmly adsorbs PCB compounds (Steen et al. 1978) than a minerogenic lake sediment. The stronger adsorption of PCBs to the sludge particles results in a reduced availability of the compounds to benthic macroinvertebrates, i.e. the equilibrium partitioning of PCBs between macroinvertebrates and sediment shifts towards the sediment.

Adult chironomids (> 90% Chironominae, Chironomini limnic and particle feeding chironomids) sampled near the sewage plant contained 0.251 ug PCBs/g fresh weight (n=5, SD 0.018) or 8.9 ug/g extractable fat (SD 0.9). The chironomid population was estimated to 9 900 larvae/m<sup>2</sup> (n=7, SD 1 300). Using the estimate and average weight of adult chironomids, approximately 20 ug PCBs/m<sup>2</sup>·year would be transported from aquatic to terrestrial environments. In this way, aquatic insects could act as a link in the transport of organochlorine residues between aquatic and terrestrial environments and mediate in the uptake of the compounds by terrestrial predators. Although sediments of lakes and water courses are thought to be the ultimate sink for persistent pollutants, remobilization of the compounds is possible which results in a transfer to the terrestrial food web.

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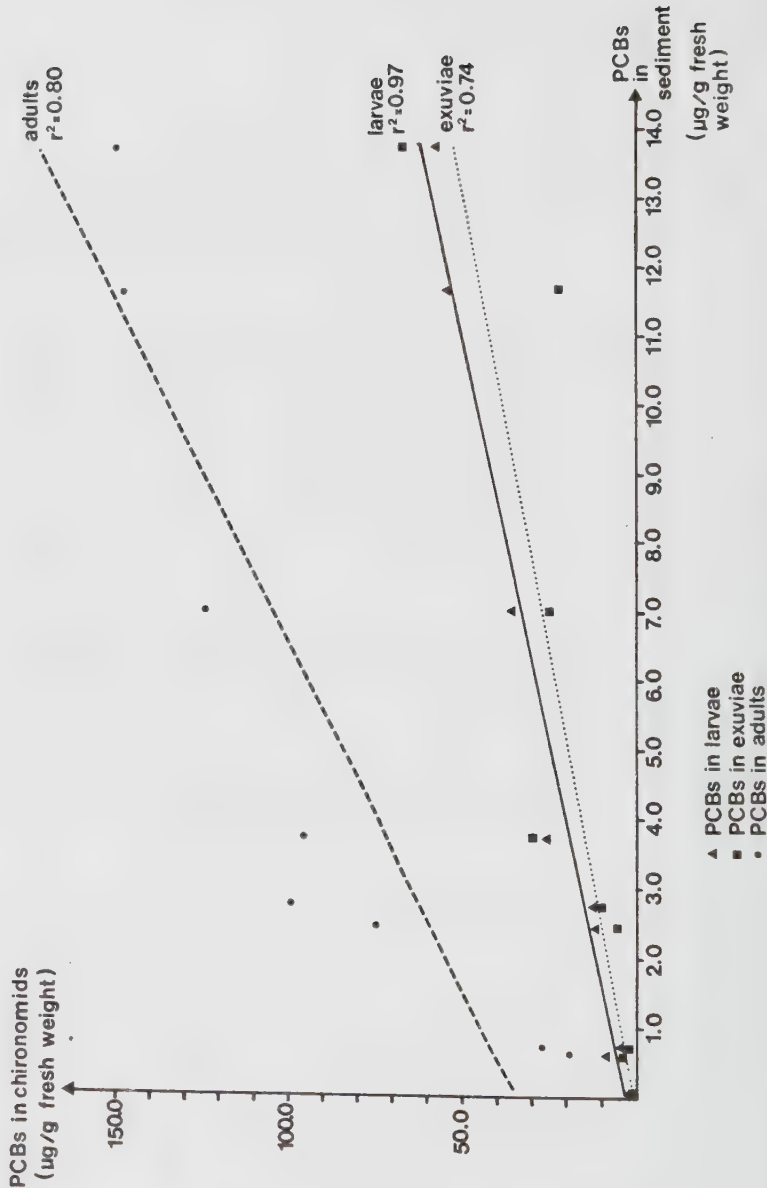
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| SEDIMENT            |                     | CHIRONOMIDS         |                   |                     |                   |                   |                   |
|---------------------|---------------------|---------------------|-------------------|---------------------|-------------------|-------------------|-------------------|
|                     |                     | Larvae              |                   | Adults              |                   | Exuviae           |                   |
| ug/g fresh weight   | ug/g dry weight     | ug/g fresh weight   | ug/g extract. fat | ug/g fresh weight   | ug/g extract. fat | ug/g fresh weight | ug/g extract. fat |
| <u>LABORATORY</u>   |                     |                     |                   |                     |                   |                   |                   |
| 0.005               | 0.027               | 0.054               | 4.7               | 0.221               | 7.7               | 0.071             | 5.6               |
| 0.0                 | 4.2                 | 8.6                 | 757               | 19.4                | 665               | 3.1               | 203               |
| 0.7                 | 2.9                 | 3.5                 | 302               | 26.9                | 913               | 2.0               | 170               |
| 2.4                 | 14.0                | 11.9                | 1042              | 74.3                | 2518              | 5.5               | 457               |
| 2.7                 | 13.5                | 12.0                | 1058              | 99.2                | 3409              | 10.2              | 850               |
| 3.7                 | 17.4                | 25.3                | 2220              | 95.8                | 3227              | 29.5              | 2390              |
| 7.0                 | 28.0                | 35.5                | 3583              | 124.0               | 4234              | 25.2              | 2104              |
| 11.6                | 58.9                | 54.1                | 4681              | 148.2               | 5027              | 22.2              | 1049              |
| 13.8                | 69.8                | 57.7                | 4845              | 150.3               | 5130              | 67.3              | 5514              |
| <u>FIELD</u>        |                     |                     |                   |                     |                   |                   |                   |
| 0.039<br>(SD 0.025) | 0.292<br>(SD 0.213) | 0.114<br>(SD 0.018) | 10.0<br>(SD 2.6)  | 0.251<br>(SD 0.019) | 8.9<br>(SD 0.9)   |                   |                   |

Tab 1. Concentrations of PCBs in sediment and chironomids in the laboratory and field studies.

Fig 1. Concentrations of PCBs in the two stages of chironomid development, and in exuviae, when exposed for 10 weeks to different sediment concentrations.





SEDIMENTATION OF POLYCHLORINATED BIPHENYLS (PCBs)  
IN LIMNIC AND MARINE ENVIRONMENTS.

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## Abstract

The sedimentation rates of PCBs in two southern Swedish lakes and a coastal bay in the southern Baltic were determined using sediment traps. The rates were similar at the three locations and ranged from 1.2 to 10.9  $\mu\text{g PCBs} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$  during summer. The source for PCBs in sedimenting material is probably the atmosphere. PCB concentrations in sedimenting material were higher than those in surface sediment. This may be due to recirculation of sediment-bound PCBs.

The reproducibility of collection by sediment traps was deployed simultaneously. There were no significant differences in PCB concentration of sedimenting material between traps placed in duplicate. Concentrations of PCBs in the different vessels was similar within one trap.

## 1. Introduction

Sediments of lakes and oceans act as a sink for persistent, chlorinated compounds. The mechanisms that govern the vertical transport of the compounds in the water column, their sorption or incorporation into the sediment and their redistribution to the water is, therefore, of importance for the total flow within the aquatic ecosystem.

The water solubility of most chlorinated hydrocarbon compounds, including polychlorinated biphenyls (PCBs), is low ( $<1 \text{ ug/l}$ , Hutzinger et al. 1974). However, due to the hydrophobic and adsorptive properties of these compounds (Haque and Schmedding 1976) their occurrence in natural waters are increased when associated to seston (Hamelink et al. 1971, Haque et al. 1974, Dexter and Pavlou 1978).

PCBs are associated or adsorbed to living organisms (e.g. plankton), to organic detritus as well as to inorganic particles. The compounds adsorbed to seston can be either cycled in the aquatic food web or transported to the bottom as sedimenting material. The sedimentation processes in the water column can be estimated by sediment traps (Osterroth and Smetacek 1980, Hargrave and Taguchi 1978, Zeitzchel et al. 1978) and the flux of PCBs to the sediment approximated. The information obtained may reflect the contamination situation in the overlying water in a more representative way and on a longer time scale, than would discrete sampling over short time intervals (Soutar et al. 1977).

The preliminary sources for PCBs to the environment include land runoff, industrial and municipal waste discharges and accidental spills. However, since the use of PCBs is restricted in most countries surrounding the Baltic, these sources should now be of minor importance. The global distribution of PCBs is mainly due to atmospheric transport (Beeton et al. 1979). PCBs have been detected in air (Bidleman and Olney 1974, Giam et al. 1980), in precipitation (Murphy and Rzeszutko 1977, Sundström 1982) and as dry deposition (Södergren 1972).

To measure the sedimentation rates of PCBs in aquatic environments, sediment traps were placed in three southern Swedish localities: the mesotrophic Lake Ivösjön, the eutrophic Lake Vombsjön and a southern bay of the Baltic (Hanö Bight). The reproducibility of the sediment traps was estimated and the sedimentation rate of PCBs at the different locations was compared.

## 2. Materials and methods

### 2.1 The sediment trap

The sediment trap consists of two main parts: the collecting sediment vessels, and a supporting structure of polyvinylchloride (Fig 1).

The sediment vessels, 64 tubes closed at one end, were made of glass (cleaned in acetone/hexane 1:1) to minimize binding of lipophilic substances to the vessels. The height/diameter ratio (300 mm/50 mm) of the sediment vessels was 6 which should minimize or avoid problems of resuspension of settled matter by turbulence (Gardner 1980, Blomqvist and Håkanson 1981).

The trap is of the buoy-carried, moored type. It is partially filled with small plastic balls which gives the trap buoyancy. The buoyancy combined with the function of the metal bar (Fig 1), shift the centre of gravity to a central position below the sediment trap. Thus, a horizontal position of the trap (and the openings of the sediment vessels) is maintained when the trap is moored. This is essential when estimating sedimentation by sediment traps (Blomqvist and Håkanson 1981).

The sediment trap studies were performed during the summer months when resuspension of bottom sediment is minimal (Hargrave and Taguchi 1978, Osterroth and Smetacek 1980).

### 2.2 Sampling localities

In June, 1980, two sediment traps were positioned at 67 m depth in Hanö Bight, a bay of the southern Baltic (Fig 2). Hanö Bight

is normally stratified during summer with a thermocline at 20 to 30 m. The character of the bight has been described elsewhere (Persson 1977, 1982). The traps were positioned about 100 m apart and 5 m above the bottom. In May, 1981, the study was repeated with one trap.

Vombsjön is a shallow (maximum depth of about 15 m), eutrophic lake situated in southern Sweden. About 70% of the catchment area is agricultural. The lake is usually total circulated. Water chemistry, phytoplankton biomass and primary production is described in detail by Gelin (1975). In April, 1980, two sediment traps were positioned in the deepest part of the lake, 2 m above the bottom and about 30 m apart.

In May, 1981, two sediment traps were suspended in Ivösjön at 48 m depth, 2 m above the bottom and 50 m apart. Ivösjön is a mesotrophic lake with a maximum depth of about 50 m. The watershed area consists mainly of agricultural land in the south and forest area in the north. The lake is usually stratified in the summer, with a thermocline at 15 m. Water chemistry, phytoplankton biomass and primary production has been described by Hamrin (1980). In May, 1982, the study was repeated with one trap.

The sediment traps were exposed for about 3 months. Seston and surface sediment were sampled at the beginning and end of the sampling period. Seston was sampled with nets (mesh sizes 10, 40 and 100  $\mu$ m) and the samples were pooled. Surface sediment was taken with a Kajak-type corer (Berggren 1972). The upper 1 cm of the sediment core was sliced off and the PCB and DDE content determined.

### 2.3 Analytical methods

Extraction of PCBs and DDE of the sedimenting material was performed in the sediment vessels after the overlying water had been removed. 20 ml of acetone was added and the vessels shaken for 10 minutes in a shaking-apparatus and treated in an ultrasonic bath for 10 minutes. 10 ml of hexane was added and the shaking and ultrasonic treatment was repeated. The aliquots were then left for 24 hours.

80 ml of 2% NaCl was added and the hexane was drawn off. The sediment aliquots were then washed with 2 x 5 ml of hexane, the solvents combined and gently evaporated to 1 ml with purified air. Solvent controls were obtained by treating clean sediment vessels similarly to the sedimenting material.

Extraction of the residues from seston and surface sediment, clean-up of the extracts and analysis by gas chromatography were performed according to Södergren (1973). The minimal detectable quantity (MDQ) for PCBs (Clophen A 50) was 0.2 ng and for individual PCB compounds 45 pg. MDQ for DDE was 36 pg.

Dry weight content and loss on ignition in sedimenting material, seston and surface sediment were carried out according to standard procedures (Svensk Standard 1981).

Analysis of the plankton species in the sedimenting material was performed by microscopy. The content of detritus, dead and living algae in the material was estimated.

### 3. Results

#### 3.1 Sampling and precision of the sediment traps

The sediment traps were placed in duplicate to compare sampling reproducibility.

Of the 64 vessels in the trap, 20 were chosen at random from each sediment trap from Lake Ivösjön 1981. One trap collected 530 mg sedimented dry material per sediment vessel, the other 491 mg (Tab 1). The difference was significant ( $P < 0.001$ , single classification ANOVA, Sokal and Rohlf 1969), with 72.7% of the variance explained by between trap comparison and 27.3% by within trap comparison (between the sediment vessels).

The dry weight of the sedimenting material in Lake Ivösjön was in 1981 significantly higher ( $P < 0.001$ , single classification ANOVA) than in 1982 (Tab 1). In this case 85% of the variance was explained

by between trap comparison (of the different years) and 15% within the traps.

In 1981 the sedimentation rates in Lake Ivösjön, as measured by the two sediment traps were 91 and 84 g dry material·m<sup>-2</sup>·month<sup>-1</sup>, respectively (Tab 1). In 1982, the sedimentation rate was 70 g·m<sup>-2</sup>·month<sup>-1</sup>. The loss on ignition in the sedimenting material of both traps in 1981 was 18.5%, and for the one trap in 1982 it was 22.5%. The loss on ignition in seston in 1981 and 1982 was 60.1% and 69.6% respectively and in surface sediment, 12.0%.

The amounts of sedimenting material (as dry weight) was higher in Lake Vombsjön than in Lake Ivösjön (Tab 1). The loss on ignition of the sedimenting material was 20.9% and 21.3%.

In Hanö Bight, one sediment trap was lost in 1980 and one in 1981. In 1980, the remaining trap collected 2.05·10<sup>3</sup> mg dry matter per vessel (Tab 1). About 20 sediment vessels in this trap were destroyed due to unknown reasons. The sedimentation rate in Hanö Bight was 4.3·10<sup>2</sup> g·m<sup>-2</sup>·month<sup>-1</sup>. The loss on ignition was 12.7% in sedimenting material, 26.6% in seston and 7.8% in the surface sediment.

Microscopic analysis of the sedimenting material in Lake Ivösjön revealed that in 1981 and 1982, diatoms (Fragilaria crotonensis, Asterionella formosa, and Rizhosolenia longiseta) dominated the samples. Both living algae and frustules were found. Fresh green algae, dominated by Staurostrum spp., were recorded. The dominating part of the algae was planktonic. Few benthic forms were found. The lower part of the sedimenting material in the sediment vessels (about 5 mm of material was deposited in the vessels) was dominated by detritus.

In the sedimenting material of Lake Vombsjön, diatoms (e.g. Melosira spp.), blue-green algae (e.g. Microcystis aeruginosa and Aphanizomenon flos-aquae) and the green algae Pediastrum duplex and P. boryanum dominated. The latter species are known to be benthic. Detritus was found at all levels in the sediment vessels.



### 3.2 Sedimentation of PCBs

Ten sediment vessels were chosen at random from each of the two sediment traps from Lake Ivösjön in 1981. The sedimenting material contained 61 ng PCBs/g dry weight and 65 ng/g dry weight (Tab 2). The difference in PCB concentration of the sedimenting material between the two traps was not significant ( $P > 0.05$ , single classification ANOVA). 4.9% of the variance was explained by between trap comparison and 95.1% within the traps.

In 1982, significantly higher concentration of PCBs was recorded in the sedimenting material (161 ng PCBs/g dry weight,  $P < 0.05$ , t-test, Tab 2), compared to the mean value for 1981.

The PCBs/DDE ratio ( $\frac{\text{ng PCBs/g dry weight}}{\text{ng DDE/g dry weight}}$ ) was between 25 and 55 for sedimenting material in 1981 and 1982 (Tab 2). For seston, the ratio was 24 and for surface sediment, 11. Surface sediment contained 22.0 ng PCBs/g dry weight.

The sedimentation rate of PCBs in 1981 was 5.6 and 5.1  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ , using values from the two sediment traps. In 1982, the sedimentation rate of PCBs was 10.9  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ .

In Lake Vombsjön, the sedimentation rates of PCBs were 1.2 and 7.7  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$  (Tab 2). The sedimenting material contained less PCBs compared to Lake Ivösjön. The PCBs/DDE ratio in sedimenting material was below 1 and in the surface sediment it was 6. The surface sediment contained 7.9 ng PCBs/g dry weight.

The sedimentation rate of PCBs in Hanö Bight was 4.8  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$  and the sedimenting material contained 11.2 ng PCBs/g dry weight. The PCBs/DDE ratio in the sedimenting material was 21. DDE was not detectable in surface sediment.

Besides PCBs and DDE, DDD and DDT were recorded in the sedimenting material and surface sediment from Lake Ivösjön.

#### 4. Discussion

The sedimentation rates of PCBs were similar in the three environments studied. The rates seemed to be independent of location, depth of trap position or amount of sedimenting material. In the Kiel Bight (southern part of the Baltic), the sedimentation rate of PCBs in 1975-77 was between 2 and 10  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$  (Osterroth and Smetacek 1980). This was almost identical to the sedimentation rates of my study. The similar sedimentation rates of PCBs for the different localities strongly indicates that the source of PCBs was the same, namely the atmosphere. The suggestion is further supported by the deposition rates of PCBs in air-borne fallout over southern Sweden (0.6-10.5  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ , Södergren 1972).

When the rate of sedimentation and the quality of the sedimenting material for Lake Vombsjön was compared to those of Lake Ivösjön and Hanö Bight several differences were observed: 1. The sedimentation rate and amounts of sedimenting material were considerably higher in Lake Vombsjön. 2. In Lake Vombsjön, the organic content of the sedimenting material (as measured by the loss on ignition) was similar to that of the surface sediment. This was not the case in Lake Ivösjön or Hanö Bight, where the organic content of sedimenting material was higher than in surface sediment. 3. The PCBs/DDE ratios of the sedimenting material were low in Lake Vombsjön and similar to the ratio for surface sediment. In contrast, the PCBs/DDE ratios were considerably higher in sedimenting material from Lake Ivösjön and Hanö Bight and similar to the ratios for seston from Lake Ivösjön. PCBs/DDE ratios in the surface sediment of Lake Ivösjön were considerably lower. 4. Benthic algae were one of the three dominating species in material of the sediment vessels from Lake Vombsjön. This was not the situation in Lake Ivösjön where planktonic diatoms dominated.

These four observations suggest that the sedimenting material in Lake Vombsjön was a result of total sedimentation; i.e. net deposition plus a dominance of resuspended material from the bottom sediment (Blomqvist and Håkanson 1981). This was further supported

by the character of Lake Vombsjön as a well-mixed, shallow lake. On the other hand, the four observations suggest that sedimentation of material in Lake Ivösjön and Hanö Bight was a result of net deposition which is important when estimating the actual flux of PCBs to the sediment. However, PCBs 'available' for sedimentation seems to be limited, since the sedimentation rates were nearly the same for the three localities.

Osterroth and Smetacek (1980) observed that the highest sedimentation rates of PCBs in the year occur during the summer months when the sedimentation of seston is minimal. Consequently, the sedimentation rates of PCBs determined in this study would be the optimal for the year. A maximal input of PCBs is, therefore, to be expected to the benthic, particle-feeding fauna (like molluscs, polychaetes, oligochaetes and limnic insects) when both growth and biomass are high. The highest exposure of PCBs to the profundal, bottom community during the year will occur in the summer, when PCB sedimentation is maximal and seston sedimentation minimal. This will lead to a concentration of PCBs in seston and thus a maximal uptake in particle-feeders. The result will thus be a fast recycling of the compounds in the food-web, when the particle-feeders are consumed by predators, like fish (e.g. pope (Acerina cernua), bream (Abramis brama) and flounder (Platichthys flesus)).

The reproducibility of the sediment traps was estimated in 1981 in Lake Ivösjön. The difference in sampling of sedimenting material between the traps was significant. This may be due to small depth variations in the positioning of the traps or to bottom currents, although the traps were positioned only 50 m apart. However, the differences in concentrations of PCBs in dry material between the traps were found not to be significant. The reproducibility of the traps is therefore concluded to be satisfactory, at least for measuring PCB sedimentation.

PCB concentrations in the sedimenting material of the different vessels within the traps deviated with 10 and 15 ng/g from the mean (61 and 65 ng/g). This is an acceptable deviation which may be due to differences in extraction efficiency in the vessels.

The differences in amounts of sedimenting material and thus concentrations of PCBs between the different years in Lake Ivösjön was probably caused by natural variations like phytoplankton biomass, break-down rates of seston and different input of allochthonous material.

The concentrations of PCBs in the surface sediments of the three localities were lower compared to those of sedimenting material. This was also the case for Kiel Bight (Osterroth and Smetacek 1980). This may have been caused by a higher overall input of PCBs during recent years, but the restrictions on PCB use make this rather improbable. However, recent studies have shown that PCBs deposited in the sediment are mobile and can be recycled back to the water (Södergren and Larsson 1982, Larsson, in press). The lower sediment concentrations of PCBs compared to those of sedimenting material indicate the same. An interesting question arises: Do sediments of lakes and oceans actually act as a 'source' for PCBs?

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| LOCATION, YEAR         | SEDIMENT TRAP                                           |                         |                                                                     | SESTON | SURFACE SEDIMENT       |
|------------------------|---------------------------------------------------------|-------------------------|---------------------------------------------------------------------|--------|------------------------|
|                        | Amount of dry material<br>(mg)                          | Loss of ignition<br>(%) | Sedimentation rates<br>(g dw·m <sup>-2</sup> ·month <sup>-1</sup> ) |        |                        |
| Lake Ivösjön, 1981, 1  | 530<br>(n=20, SD 15)                                    | 18.5<br>(n=10, SD 0.7)  | 91                                                                  | 60.1   | 12.0<br>(n=13, SD 0.7) |
| Lake Ivösjön, 1981, 2  | 491<br>(n=20, SD 15)                                    | 18.5<br>(n=10, SD 0.3)  | 84                                                                  |        |                        |
| Lake Ivösjön, 1982     | 431<br>(n=20, SD 16)                                    | 22.5<br>(n=10, SD 0.3)  | 70                                                                  | 69.6   |                        |
| Lake Vombsjön, 1980, 1 | 10.8·10 <sup>3</sup><br>(n=20, SD 1.5·10 <sup>3</sup> ) | 20.9<br>(n=10, SD 1.2)  | 2.3·10 <sup>3</sup>                                                 | 77.9   | 20.2<br>(n=4, SD 1.1)  |
| Lake Vombsjön, 1980, 2 | 15.8·10 <sup>3</sup><br>(n=20, SD 2.6·10 <sup>3</sup> ) | 21.3<br>(n=10, SD 3.0)  | 3.3·10 <sup>3</sup>                                                 |        |                        |
| Hanö Bight, 1980       | 2.05·10 <sup>3</sup><br>(n=5, SD 0.22·10 <sup>3</sup> ) | 12.7<br>(n=5, SD 1.7)   | 4.3·10 <sup>2</sup>                                                 | 26.6   | 7.8<br>(n=3, SD 1.1)   |

Tab 1 Amount of sedimenting material, loss on ignition and sedimentation rates in Lake Ivösjön, Lake Vombsjön and Hanö Bight 1980-82. Loss on ignition in seston and surface sediment are shown. dw= dry weight

| LOCATION, YEAR         | SEDIMENT TRAP         |                                                                                             |                       |                                  |                                                 | SESTON             |                                  |                        | SURFACE SEDIMENT      |                                  |  |
|------------------------|-----------------------|---------------------------------------------------------------------------------------------|-----------------------|----------------------------------|-------------------------------------------------|--------------------|----------------------------------|------------------------|-----------------------|----------------------------------|--|
|                        | PCBs<br>(ng/g dw)     | Sedimentation<br>rates of PCBs<br>( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ ) | DDE<br>(ng/g dw)      | $\frac{\text{PCBs}}{\text{DDE}}$ | PCBs<br>(ng/g dw)                               | DDE<br>(ng/g dw)   | $\frac{\text{PCBs}}{\text{DDE}}$ | PCBs<br>(ng/g dw)      | DDE<br>(ng/g dw)      | $\frac{\text{PCBs}}{\text{DDE}}$ |  |
| Lake Ivösjön, 1981, 1  | 61<br>(n=10, SD 10)   | 5.6                                                                                         | 1.1<br>(n=10, SD 0.2) | 55                               | $1.3 \cdot 10^3$<br>(n=6, SD $0.7 \cdot 10^3$ ) | 53<br>(n=6, SD 25) | 24                               | 22.0<br>(n=13, SD 9.1) | 2.0<br>(n=13, SD 1.2) | 11                               |  |
| Lake Ivösjön, 1981, 2  | 65<br>(n=10, SD 15)   | 5.1                                                                                         | 1.2<br>(n=10, SD 0.6) | 52                               |                                                 |                    |                                  |                        |                       |                                  |  |
| Lake Ivösjön, 1982     | 161<br>(n=10, SD 38)  | 10.9                                                                                        | 6.5<br>(n=10, SD 1.1) | 25                               |                                                 |                    |                                  |                        |                       |                                  |  |
| Lake Vombsjön, 1980, 1 | 0.5<br>(n=7, SD 0.3)  | 1.2                                                                                         | 1.8<br>(n=7, SD 0.5)  | 0.5                              | n.a.                                            | n.a.               | -                                | 7.9<br>(n=4, SD 0.8)   | 1.4<br>(n=4, SD 0.2)  | 6                                |  |
| Lake Vombsjön, 1980, 2 | 2.3<br>(n=6, SD 1.1)  | 7.7                                                                                         | 3.6<br>(n=6, SD 1.3)  | 0.6                              |                                                 |                    |                                  |                        |                       |                                  |  |
| Hanö Bight, 1980       | 11.2<br>(n=7, SD 3.5) | 4.8                                                                                         | 0.5<br>(n=7, SD 0.2)  | 21                               | n.a.                                            | n.a.               | -                                | 0.9<br>(n=5, SD 0.3)   | n.d.                  | -                                |  |

Tab 2 Sedimentation rates of PCBs, concentrations of PCBs and DDE in sedimenting material, seston and surface sediment of Lake Ivösjön, Lake Vombsjön and Hanö Bight. PCBs/DDE ratios are also given. dw= dry weight, n.a.= not analyzed, n.d.= not detected

Fig 1. Sediment trap for  
determination of PCBs  
in sedimenting material.

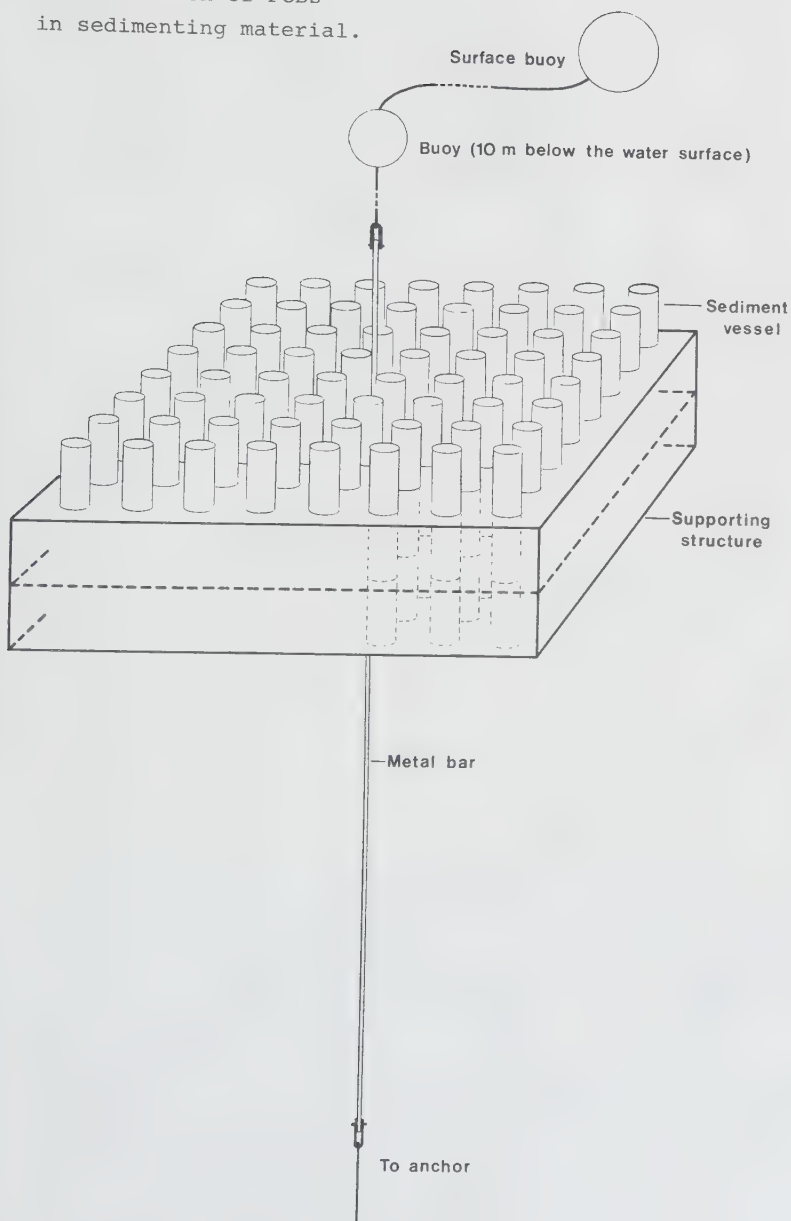
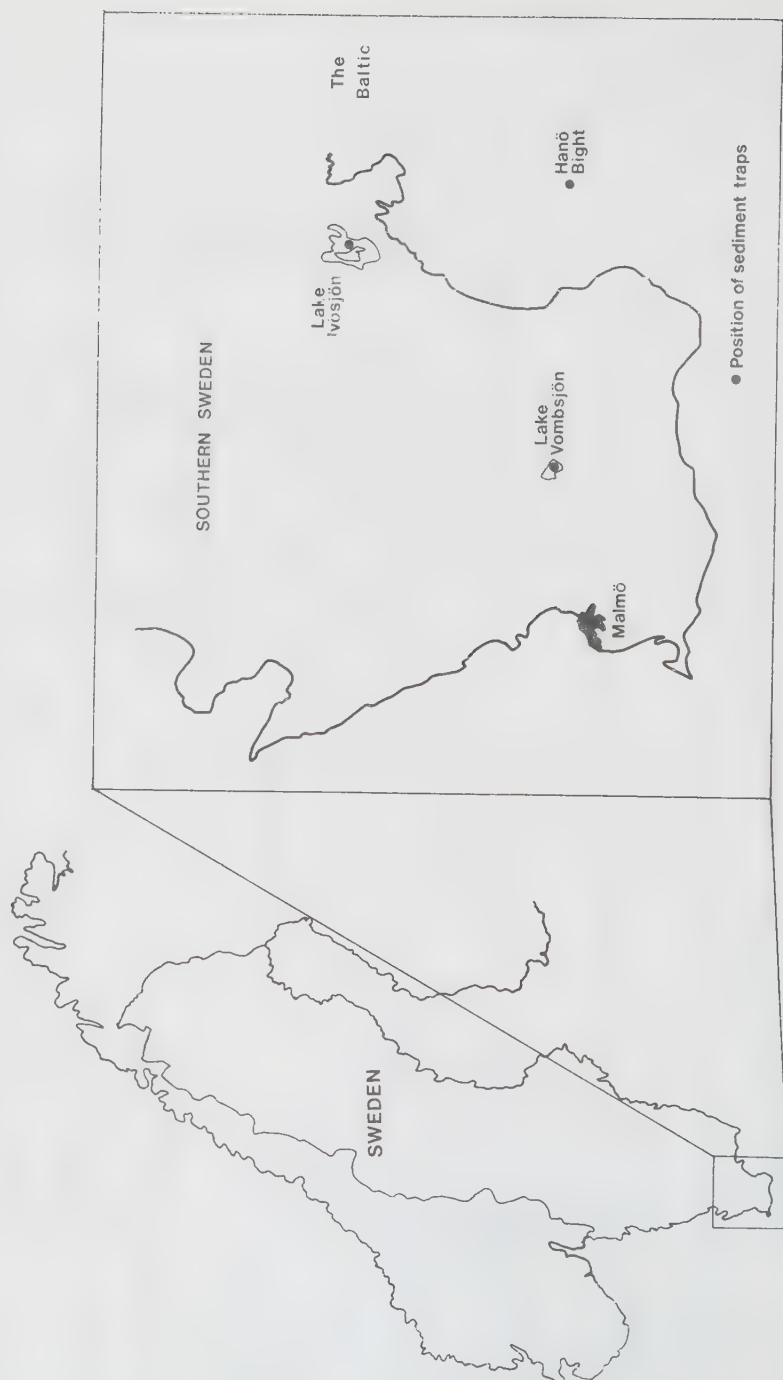


Fig 2 Localities where PCBs in sedimenting material were determined.











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